

(19) World Intellectual Property Organization
International Bureau



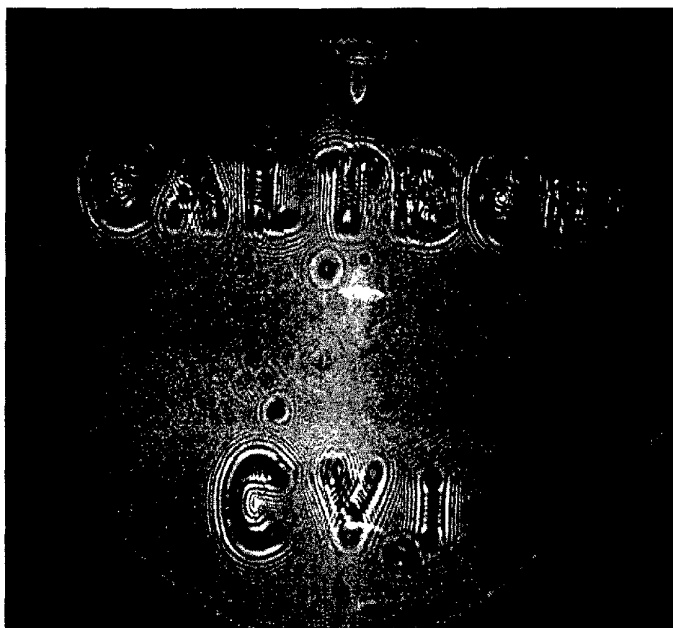
(43) International Publication Date
15 November 2001 (15.11.2001)

PCT

(10) International Publication Number
WO 01/86647 A2

- (51) International Patent Classification⁷: **G11B 7/24**
- (21) International Application Number: PCT/US01/15419
- (22) International Filing Date: 10 May 2001 (10.05.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/203,317 10 May 2000 (10.05.2000) US
- (71) Applicant: **CALIFORNIA INSTITUTE OF TECHNOLOGY** [US/US]; 1200 East California Boulevard, Mail Stop 201-85, Pasadena, CA 91125 (US).
- (72) Inventors: **SANDSTEDT, Christian, A.**; 680 S. Marengo Avenue, #10, Pasadena, CA 91106 (US). **JETHMALANI, Jagdish, M.**; 85 N. Madison Avenue, #48, Pasadena, CA 91101 (US). **KORNFELD, Julia, A.**; 371 S. Berkeley Avenue, Pasadena, CA 91107 (US). **GRUBBS, Robert, H.**; 1700 Spruce Street, South Pasadena, CA 91030 (US).
- (74) Agents: **PECK, John, W.** et al.; Christie, Parker & Hale, LLP, P.O. Box 7068, Pasadena, CA 91109-7068 (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— *without international search report and to be republished upon receipt of that report*
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: PHASE CONTRAST VARIATION OF A PHOTO-INDUCED REFRACTIVE MATERIAL



(57) Abstract: The present invention relates to compositions useful for optically recording or storing data by stimulating a composition having a refraction modulating composition, where a stimulated region of the composition represents one kind of data and a non-stimulated region of the composition represents another kind of data. The present invention also relates to methods of optically recording data utilizing the compositions of the present invention, as well as to optical data storage devices and optical data storage elements which utilize the optical data storage compositions of the invention.



WO 01/86647 A2

1

PHASE CONTRAST VARIATION OF A PHOTO-INDUCED REFRACTIVE MATERIAL

FIELD OF INVENTION

5

This invention relates generally to photo-induced refractive media for holographic data storage; and more particularly to a photo-induced refractive polymeric composition for use as a high-density storage medium for optically based data storage devices.

BACKGROUND

10

Optical systems provide extremely fast and effective means for processing information. In a typical system, an image comprising data is modulated into a coherent light beam. This can be performed by a spatial light modulator placed in the beam. The resulting spatially modulated beam then enters a series of optical elements which filter and process the image, and a detector records the final output. The list of applications for these systems is long, including image and data processing, pattern recognition, optical computation, and high density data storage systems such as holographic data storage systems.

15

20

Despite the enormous promise these optical data storage systems hold, finding the optimal material for the application of holography and other optical techniques to data storage is a challenging undertaking, and the quantitative testing and comparison of a variety of different materials continues to make up a significant part of the research effort into optical data storage. There are a number of properties a good optical data storage material should have, including: excellent optical quality, high recording fidelity, high dynamic range, low scattered light, high sensitivity, and non-volatile storage.

25

For example, with regard to excellent optical quality, a high resolution data page with as many as a million pixels encoding digital data must be imaged through the material and onto the detector array, pixel for pixel. This requires very good homogeneity, and optical quality surfaces.

High recording fidelity is important because the material must faithfully record the data beam amplitude so that this high quality image can be reconstructed when the data is read out.

30

High dynamic range is important because the larger the amount of data that is recorded in a common volume of material, the weaker each bit of data becomes; the signal strength scales as the inverse square of the amount of data, and is limited ultimately by the ability of the material to respond to optical exposure with the refractive index modulation that records the data. The greater is the materials ability to respond, i.e. the greater its dynamic range, the more data that can be recorded, and ultimately, the greater the density of data that can be stored.

35

1 The light scattering properties of the material are important because the ultimate lower
limit to the strength of optical materials that are useful for data storage is determined by noise
from readout beam scattering. Thus, scattered light also limits storage density.

5 High sensitivity is likewise important because to store data in the material at a reasonable
data rate, the material should respond to the recording beams with high sensitivity.

10 Finally, non-volatile storage is perhaps of greatest concern because the material must
retain the stored data for a time consistent with a data storage application, and should do so in
the presence of the light beams used to read the data. For write-once read-many storage, an
irreversible material (such as a photopolymer) can be used, which provides stable recording once
15 exposed. If a reversible material is chosen in order to implement erasable/re-writable data
storage, the requirement for nonvolatility is in conflict with that for high sensitivity unless a
nonlinear writing scheme, such as two-color gated recording is used.

20 There are several ways to optically store and retrieve information. For example, some of
the materials tested for data storage possess refractive components such as monomers which
crosslink, while others have mesogens attached to the main chain or side chain polymers, while
yet others have photochromic or thermochromic groups attached to the polymer chains.
However, the materials which show the most promise for data storage have been photorefractive
materials.

25 The conventional photorefractive effect was first observed in inorganic materials, e.g.
barium, titanate and lithium niobate. Since the demonstration of the first organic polymer based
photorefractive (PR) system in 1991 by Ducharme et al., this class of materials has been
developed to a point where they have now equaled or surpassed many of the performance
characteristics of both organic and inorganic photorefractive crystals. See, S. Ducharme, J. C.
Scott, R. J. Twieg and W. E. Moerner, *Phys. Rev. Lett.* 66, 1846 (1991). Together with the low
30 cost and versatility of organic polymer based systems this makes them highly attractive for
commercial applications in optical data storage and optical data processing. Recently, a
conventional photorefractive polymer has been shown to exhibit 86% steady state diffraction
efficiency moving photorefractive polymers further toward implementation. See, e.g., K.
Meerholz, B. L. Volodin, Sandalphon, B. Kippelen and N. Peyghambarian, *Nature*, 371,497
35 (1994); and B. Kippelen, Sandalphon, N. Peyghambarian, S. R. Lyon, A. B. Padias and H. K.
Hall Jr., *Electronic. Lett.* 29, 1873 (1993). However, several groups have reported this to be a
capricious and unstable system which suffers from non-trivial sample preparation, stringent
storage requirements (low humidity and dust free environment), and a risk of short device
lifetimes. This system has also since been reported by many groups to be extremely difficult to
synthesize with good optical quality due to the crystallization of the dye from the matrix. See,
e.g., W. E. Moerner, C. Poga, Y. Jia and R. J. Twei, *Organic Thin Films for Photonics*

1 Applications (OSA Technical Digest Series), 21, 331 (1995); C. Poga, R. J. Twieg and W. E.
Moerner. Organic Thin Films for Photonics Applications (OSA Technical Digest Series), 21,342
(1995); and B. G. Levi, Physics Today, 48,1, 17 (1995). In addition, most conventional
5 holographic data storage media utilize a glassy matrix to disperse the photorefractive monomers.
However, in these systems crosslinking of monomers followed by monomer diffusion in a glassy
matrix creates volume shrinkage. This is a problem when multiple data is stored at different
angles. In an ideal material, then, volume shrinkage of the material would be avoided. In such
a circumstance, the first few bits of data stored in the medium lose their resolution due to the
shrinkage.

10 Other examples of prior art optical storage systems and compositions can be found, for
example, in U.S. Patent Nos. 4,172,474; 4,944,112; 5,173,381; 5,470,662; 5,858,585; 5,892,601;
5,920,536; 5,943,145; and 6,046,290. However, each of these systems and compositions contains
limitations that make the development of new materials for optical data storage necessary.

15 Accordingly there is a need in the field of optical data storage for new more efficient,
economical and hardy optical data storage materials.

SUMMARY

20 The present invention is directed in part to a composition, method and system for
recording or storing data by stimulating a composition having a refraction modulating
composition dispersed in a polymer matrix wherein the phase contrast is purely the result of the
crosslinking of the macromers followed by macromer diffusion, such that there is a null point
where the volume shrinkage is overcome by the macromer diffusion. Applicants discovered that
since there is a refractive index contrast between the matrix and the macromer, a composition
comprising a refraction modulating composition dispersed in a polymer matrix can be stimulated
25 in particular patterns and these patterns can be used for data recording and storage.

30 Accordingly, in one embodiment the invention is directed to a composition for data
storage comprising a first polymer matrix and a refraction modulating composition dispersed
therein. Any refraction modulating composition capable of stimulus-induced polymerization can
be suitably used, such as photorefractive, photo-induce refractive, photo-addressable, and liquid
crystal compositions. In such an embodiment, the stimulated region of the composition
represents one kind of data and a non-stimulated region of the composition represents another
kind of data.

35 The invention is also directed to a method of recording data comprising stimulating a
composition, wherein the composition comprises a first polymer matrix and a refraction
modulating composition dispersed therein wherein the refraction modulating composition is
capable of stimulus-induced polymerization, and wherein a stimulated region of the composition

1 represents one kind of data and a non-stimulated region of the composition represents another
kind of data.

The invention is also directed to apparatuses for recording or storing data by stimulating
a composition having a refraction modulating composition as described above, where a
5 stimulated region of the composition represents one kind of data and a non-stimulated region of
the composition represents another kind of data.

BRIEF DESCRIPTIONS OF THE DRAWINGS

10 These and other features and advantages of the present invention will be better understood
by reference to the following detailed description when considered in conjunction with the
accompanying drawings wherein:

Figure 1a is a schematic of a disk of the present invention being irradiated in the center
followed by irradiation of the entire disk to "lock in" the data.

15 Figure 1b is a schematic of a disk of the present invention being irradiated in the center
followed by irradiation of the entire disk to "lock in" the data.

Figure 1c is a schematic of a disk of the present invention being irradiated in the center
followed by irradiation of the entire disk to "lock in" the data.

Figure 1d is a schematic of a disk of the present invention being irradiated in the center
followed by irradiation of the entire disk to "lock in" the data.

20 Figure 2a illustrates the prism irradiation procedure that is used to quantify the refractive
index changes after being exposed to various amounts of irradiation.

Figure 2b illustrates the prism irradiation procedure that is used to quantify the refractive
index changes after being exposed to various amounts of irradiation.

25 Figure 2c illustrates the prism irradiation procedure that is used to quantify the refractive
index changes after being exposed to various amounts of irradiation.

Figure 2d illustrates the prism irradiation procedure that is used to quantify the refractive
index changes after being exposed to various amounts of irradiation.

30 Figure 3a shows unfiltered Moiré fringe patterns of an inventive disk of the optical data
storage composition. The angle between the two Ronchi rulings was set at 12° and the
displacement distance between the first and second Moiré patterns was 4.92 mm.

Figure 3b shows unfiltered Moiré fringe patterns of an inventive disk of the optical data
storage composition. The angle between the two Ronchi rulings was set at 12° and the
displacement distance between the first and second Moiré patterns was 4.92 mm.

35 Figure 4 is a Ronchigram of an inventive disk of the optical data storage composition.
The Ronchi pattern corresponds to a 2.6 mm central region of the disk.

1 Figure 5a is a schematic illustrating a second mechanism whereby the formation of the second polymer matrix modulates an optical property by altering the disk shape.

 Figure 5b is a schematic illustrating a second mechanism whereby the formation of the second polymer matrix modulates an optical property by altering the disk shape.

5 Figure 5c is a schematic illustrating a second mechanism whereby the formation of the second polymer matrix modulates an optical property by altering the disk shape.

 Figure 5d is a schematic illustrating a second mechanism whereby the formation of the second polymer matrix modulates an optical property by altering the disk shape.

10 Figure 6a are Ronchi interferograms of a disk of the optical data storage composition before and after laser treatment.

 Figure 6b are Ronchi interferograms of a disk of the optical data storage composition before and after laser treatment.

 Figure 7 is the corresponding Ronchi interferogram of a photopolymer film in which "CALTECH" and "CVI" were written using the 325 nm line of He:Cd laser.

15 Figure 8a is a schematic of an optical data storage apparatus according to the present invention.

 Figure 8b is a schematic of an optical data storage apparatus according to the present invention.

20 Figure 8c is a schematic of an optical data storage apparatus according to the present invention.

 Figure 9 is a schematic of a holographic data storage apparatus according to the present invention.

 Figure 10a is a schematic illustrating the operation of a holographic data storage system.

 Figure 10b is a schematic illustrating the operation of a holographic data storage system.

25 Figure 10c is a schematic illustrating the operation of a holographic data storage system.

 Figure 10d is a schematic illustrating the operation of a holographic data storage system.

 Figure 11 is a photograph of a section of photopolymerized film.

 Figure 12 is a schematic of a data storage unit according to the present invention.

30 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

 The present invention relates to stimulating a composition comprising a refraction modulating composition dispersed in a polymer matrix and using stimulating patterns in data recording and storage.

35 Figures 1a to 1d illustrates one inventive embodiment of the current invention in which the refractive index of a particular disk of photo reflective material **10** is changed by light induced polymerization. Once the data is input into the disk **10** as phase contrast variations of the photo

1 reflective material, the data can then be "locked-in" via flood irradiation of the entire disk **10**.
In the embodiment shown in Figure 1a, the optical data storage element **10** comprises a first
polymer modulating composition (FPMC) **12** having a refraction modulating composition (RMC)
14 dispersed therein. The FPMC **12** forms the optical element framework and is generally
5 responsible for many of its material properties. The RMC **14** may be a single compound or a
combination of compounds that is capable of stimulus-induced polymerization, preferably photo-
polymerization. As used herein, the term "polymerization" refers to a reaction wherein at least
one of the components of the RMC **14** reacts to form at least one covalent or physical bond with
either a like component or with a different component. The identities of the FPMC **12** and the
10 RMC **14** will depend on the requirements of the end use data element **10**. However, as a general
rule, the FPMC **12** and the RMC **14** are selected such that the components that comprise the
RMC **14** are capable of diffusion within the FPMC **12**, e.g., a loose FPMC **12** will tend to be
paired with larger RMC components **14** and a tight FPMC **12** will tend to be paired with smaller
RMC **14**.

15 As shown in Figure 1b, upon exposure to an appropriate energy source **16** (e.g., heat or
light), the RMC **14** typically forms a second polymer matrix **18** in the exposed region **20** of the
optical data storage element **10**. The presence of the second polymer matrix **18** changes the
material characteristics of this region **20** of the optical element **10** to modulate its refraction
capabilities. In general, the formation of the second polymer matrix **18** typically increases the
20 refractive index of the affected region **20** of the optical data storage element **10**.

As shown in Figure 1c, after exposure, the RMC **14** in the unexposed region **22** will
migrate into the exposed region **20** over time. The amount of RMC **14** migration into the
exposed region **20** depends upon the frequency, intensity, and duration of the polymerizing
stimulus and may be precisely controlled. If enough time is permitted, the RMC **14** will re-
25 equilibrate and redistribute throughout the optical data storage element **10** (i.e., the FPMC **12**,
including the exposed region). When the region is re-exposed to the energy source **16**, the
RMC **14** that has since migrated into the region **20** (which may be less than if the RMC **14** were
allowed to re-equilibrate) polymerizes to further increase the formation of the second polymer
matrix **18**. This process (exposure followed by an appropriate time interval to allow for
30 diffusion) may be repeated until the exposed region **20** of the optical data storage element **10** has
been sufficiently modified to store the data of interest. The entire data storage element **10** may
then be exposed to the energy source **16** to "lock-in" the desired data by polymerizing the
remaining RMC **14** that are outside the exposed region **20** before the components **14** can migrate
into the exposed region **20**, thus forming a read-only optical data storage element **10**, as shown
35 in Figure 1d. Under these conditions, because freely diffusible RMC **14** are no longer available,

1 subsequent exposure of the optical data storage element **10** to an energy source **16** cannot further
change its optical properties.

5 The FPMC **12** is a covalently or physically linked structure that functions as an optical
data storage element **10** and is formed from a FPMC **12**. In general, the FPMC **12** comprises one
or more monomers that upon polymerization will form the FPMC **12**. The FPMC **12** optionally
10 may include any number of formulation auxiliaries that modulate the polymerization reaction or
improve any property of the data storage element **10**. Illustrative examples of suitable FPMC **12**
monomers include poly-carbonates, acrylics, methacrylates, phosphazenes, siloxanes, vinyls,
homopolymers, and copolymers thereof, and side chain and main chain mesogens, and
photochromic and thermochromic moieties, and moieties which undergo a photo-induced
15 *cis/trans* isomerization, such as, azo-benzene. As used herein, a "monomer" refers to any unit
(which may itself either be a homopolymer or copolymer) which may be linked together to form
a polymer containing repeating units of the same. If the FPMC monomer **12** is a copolymer, it
may be comprised of the same type of monomers (*e.g.*, two different siloxanes) or it may be
comprised of different types of monomers (*e.g.*, a siloxane and an acrylic).

In one embodiment, the one or more monomers that form the FPMC **12** are polymerized
and cross-linked in the presence of the RMC **14**. In another embodiment, polymeric starting
material that forms the FPMC **12** is cross-linked in the presence of the RMC **14**. Under either
20 scenario, the RMC **14** must be compatible with and not appreciably interfere with the formation
of the FPMC **12**. Similarly, the formation of the second polymer matrix **18** should also be
compatible with the existing FPMC **12**, such that the FPMC **12** and the second polymer matrix **18**
should not phase separate and light transmission by the optical data storage element **10** should
be unaffected.

As described previously, the RMC **14** may be a single component or multiple components
25 so long as: (i) it is compatible with the formation of the FPMC **12**; (ii) it remains capable of
stimulus-induced polymerization after the formation of the FPMC **12**; and (iii) it is freely
diffusible within the FPMC **12**. In one embodiment, the stimulus-induced polymerization is
photo-induced polymerization.

As described above the compositions of the current invention have numerous applications
30 in the electronics and data storage industries. The optical elements also have applications in the
medical field, such as being used as medical lenses, particularly as IOL. In such an embodiment,
the FPMC **12** and the RMC **14** are as described above with the additional requirement that the
resulting materials be biocompatible. Illustrative examples of a suitable biocompatible FPMC **12**
include: poly-acrylates such as poly-alkyl acrylates and poly-hydroxyalkyl acrylates; poly-
35 methacrylates such as poly-methyl methacrylate ("PMMA"), poly-hydroxyethyl methacrylate
("PHEMA"), and poly-hydroxypropyl methacrylate ("PHPMA"); poly-vinyls such as poly-styrene

1 and poly-N-vinylpyrrolidone ("PNVP"); poly-siloxanes such as poly-dimethylsiloxane; poly-phosphazenes, and copolymers of thereof. U.S. Patent No. 4,260,725 and patents and references cited therein (which are all incorporated herein by reference) provide more specific examples of suitable polymers that may be used to form the FPMC 12.

5 In preferred embodiments, the FPMC 12 generally possesses a relatively low glass transition temperature (" T_g ") such that the resulting optical data storage element 10 tends to exhibit fluid-like and/or elastomeric behavior, and is typically formed by crosslinking one or more polymeric starting materials wherein each polymeric starting material includes at least one crosslinkable group. Illustrative examples of suitable crosslinkable groups include but are not
10 limited to hydride, acetoxy, alkoxy, amino, anhydride, aryloxy, carboxy, enoxy, epoxy, halide, isocyno, olefinic, and oxime. In more preferred embodiments, each polymeric starting material includes terminal monomers (also referred to as endcaps) that are either the same or different from the one or more monomers that comprise the polymeric starting material but include at least one crosslinkable group, e.g., such that the terminal monomers begin and end the polymeric
15 starting material and include at least one crosslinkable group as part of its structure. Although it is not necessary for the practice of the present invention, the mechanism for crosslinking the polymeric starting material preferably is different than the mechanism for the stimulus-induced polymerization of the components that comprise the RMC 14. For example, if the RMC 14 is polymerized by photo-induced polymerization, then it is preferred that the polymeric starting
20 materials have crosslinkable groups that are polymerized by any mechanism other than photo-induced polymerization.

An especially preferred class of polymeric starting materials for the formation of the FPMC 12 is poly-siloxanes (also known as "silicones") endcapped with a terminal monomer which includes a crosslinkable group selected from the group consisting of acetoxy, amino,
25 alkoxy, halide, hydroxy, and mercapto. Because silicone elements tend to be flexible and foldable, the optical data storage elements created thereby will be much less susceptible to damage and data loss. An example of an especially preferred polymeric starting material is bis(diacetoxymethylsilyl)-polydimethylsiloxane (which is poly-dimethylsiloxane that is endcapped with a diacetoxymethylsilyl terminal monomer).

30 The RMC 14 that is used in fabricating optical data storage elements is as described above except that it has the additional requirement of biocompatibility. The RMC 14 is capable of stimulus-induced polymerization and may be a single component or multiple components so long as: (i) it is compatible with the formation of the FPMC 12; (ii) it remains capable of stimulus-induced polymerization after the formation of the FPMC 12; and (iii) it is freely
35 diffusible within the FPMC 12. In general, the same type of monomers that is used to form the FPMC 12 may be used as a component of the RMC 14. However, because of the requirement

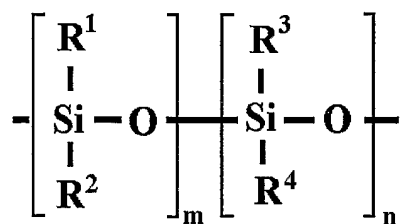
1 that the RMC 14 monomers must be diffusable within the FPMC 12, the RMC 14 monomers
generally tend to be smaller (*i.e.*, have lower molecular weights) than the monomers which form
the FPMC 12. In addition to the one or more monomers, the RMC 14 may include other
5 components such as initiators and sensitizers that facilitate the formation of the second polymer
matrix 18.

In preferred embodiments, the stimulus-induced polymerization is photo-polymerization.
In other words, the one or more monomers that comprise the RMC 14 each preferably includes
at least one group that is capable of photopolymerization. Illustrative examples of such
10 photopolymerizable groups include but are not limited to acrylate, allyloxy, cinnamoyl,
methacrylate, stibenyl, and vinyl. In more preferred embodiments, the RMC 14 includes a
photoinitiator (any compound used to generate free radicals) either alone or in the presence of
a sensitizer. Examples of suitable photoinitiators include acetophenones (*e.g.*, *a*-substituted
haloacetophenones, and diethoxyacetophenone); 2,4-dichloromethyl-1,3,5-triazines; benzoin
15 alkyl ethers; and *o*-benzoyloximino ketone. Examples of suitable sensitizers include *p*-
(dialkylamino)aryl aldehyde; *N*-alkylindolylidene; and bis[*p*-(dialkylamino)benzylidene] ketone.

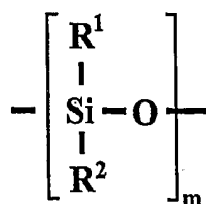
Because of the preference for flexible and foldable optical data storage elements, an
especially preferred class of RMC 14 monomers is poly-siloxanes endcapped with a terminal
siloxane moiety that includes a photopolymerizable group. An illustrative representation of such
a monomer is:



20 wherein Y is a siloxane which may be a monomer, a homopolymer or a copolymer formed from
any number of siloxane units, and X and X¹ may be the same or different and are each
independently a terminal siloxane moiety that includes a photopolymerizable group. An
illustrative example of Y include:



30 and;

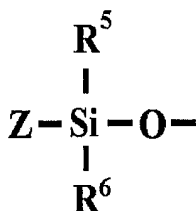


1

where m and n are independently each an integer and R¹, R², R³, and R⁴ are independently each hydrogen, alkyl (primary, secondary, tertiary, cyclo), aryl, or heteroaryl. In a preferred embodiment, R¹, R², R³, and R⁴ are each a C₁-C₁₀ alkyl or phenyl. Because RMC 14 monomers with a relatively high aryl content have been found to produce larger changes in the refractive index of the inventive lens, it is generally preferred that at least one of R¹, R², R³, and R⁴ is an aryl, particularly phenyl. In more preferred embodiments, R¹, R², and R³ are the same and are methyl, ethyl, or propyl and R⁴ is phenyl.

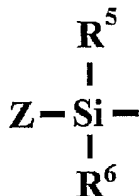
10 Illustrative examples of X and X¹ (or X¹ and X depending on how the RMC 14 polymer is depicted) are:

15



and;

20



25 respectively where R⁵ and R⁶ are independently each hydrogen, alkyl, aryl, or heteroaryl; and Z is a photopolymerizable group.

In preferred embodiments, R⁵ and R⁶ are independently each a C₁-C₁₀ alkyl or phenyl and Z is a photopolymerizable group that includes a moiety selected from the group consisting of acrylate, allyloxy, cinnamoyl, methacrylate, stibenyl, and vinyl. In more preferred embodiments, R⁵ and R⁶ are methyl, ethyl, or propyl and Z is a photopolymerizable group that includes an acrylate or methacrylate moiety.

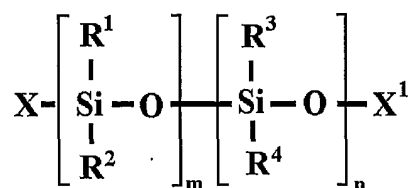
30

In especially preferred embodiments, an RMC 14 monomer is of the following formula:

35

1

5



10

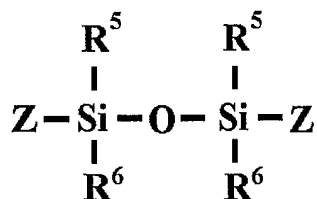
wherein X and X¹ are the same and R¹, R², R³, and R⁴ are as defined previously. Illustrative examples of such RMC 14 monomers include dimethylsiloxane-diphenylsiloxane copolymer endcapped with a vinyl dimethylsilane group; dimethylsiloxane-methylphenylsiloxane copolymer

15

endcapped with a methacryloxypropyl dimethylsilane group; and dimethylsiloxane endcapped with a methacryloxypropyldimethylsilane group.

Although any suitable method may be used, a ring-opening reaction of one or more cyclic siloxanes in the presence of triflic acid has been found to be a particularly efficient method of making one class of inventive RMC 14 monomers. Briefly, the method comprises contacting a

20



25

in the presence of triflic acid wherein R⁵, R⁶, and Z are as defined previously. The cyclic siloxane may be a cyclic siloxane monomer, homopolymer, or copolymer. Alternatively, more than one cyclic siloxane may be used. For example, a cyclic dimethylsiloxane tetramer and a cyclic methyl-phenylsiloxane trimer/tetramer are contacted with bis-methacryloxypropyltetramethyldisiloxane in the presence of triflic acid to form a dimethylsiloxane methylphenylsiloxane copolymer that is endcapped with a methacryloxypropyldimethylsilane group, an especially preferred RMC 14 monomer.

30

Although primarily photo-induced refractive compounds are discussed above, any refraction modulating composition may be used such as photorefractive, photo-addressable, and liquid crystal compositions

35

The optical data storage elements may be fabricated with any suitable method that results in a FPMC 12 with one or more components which comprise the RMC 14 dispersed therein, and wherein the RMC 14 is capable of stimulus-induced polymerization to form a second polymer matrix 18. In one embodiment, the method comprises mixing a FPMC 12 composition with a RMC 14 to form a reaction mixture; placing the reaction mixture into a mold; polymerizing the

1 FPMC 12 composition to form said optical data storage element 10; and, removing the optical data storage element 10 from the mold.

The type of mold that is used will depend on the optical data storage element being made. For example, if the optical data storage element 10 is a prism, as shown in Figures 2a to 2d, then
5 a mold in the shape of a prism is used. Similarly, if the optical data storage element 10 is a disk, as shown in Figures 1a to 1d, then a disk mold is used and so forth. As described previously, the FPMC 12 composition comprises one or more monomers for forming the FPMC 12 and optionally includes any number of formulation auxiliaries that either modulate the polymerization reaction or improve any property (whether or not related to the optical characteristic) of the
10 optical data storage element 10. Similarly, the RMC 14 comprises one or more components that together are capable of stimulus-induced polymerization to form the second polymer matrix 18. Because flexible and foldable optical data storage elements generally permit more durable elements, it is preferred that both the FPMC 12 composition and the RMC 14 include one or more silicone-based or low T_g acrylic monomers.

15 The optical data storage composition 10 can be designed into any suitable conventional data storage device. For example, one data storage device 50 is shown schematically in Figure 12. In this embodiment the optical data storage device 50 comprises a base material 52 embossed with a tracking layer 54 which serves to assist in the tracking process and provides tracking information. Any suitable material can be utilized for such a base material and tracking layer 54,
20 such as, for example a metallised Mylar sheet or even a separate optical data composition layer on a plastic substrate. In addition, the size and format of the tracks can take any suitable format, such as, for example, in one embodiment the tracks are ANSI and ISO compliant continuous composite format standards. A suitable thickness for such a layer is about 30 μm . The data storage composition 10 is then coated onto the tracking layer 54. Preferably the data storage
25 composition 10 is coated over the tracking layer 54 in a thickness suitable to store single or multiple optical patterns at varying depths. A typical thickness for such a layer is about 50 μm , however any thickness can be used, for example thicker films might be used to allow for the input of larger three-dimensional holographic data. A transparent protective outer layer 56 is then coated over the data storage composition 10 to provide durability. Any other conventional
30 coating layer may be added to the data storage device 50 described above as required by the application. For example, in case a thermal erasure process is utilized, an additional oxide layer may be necessary.

Although one combination of layers is described above with reference to Figure 12, any suitable device may be constructed such that the data storage composition 10 of the current
35 invention can be controllably exposed to a sufficient stimulus such that data can be imprinted into the data storage composition 10 and such that the data can be reliably recovered therefrom. For

1 example, the data storage unit may be disposed between a pair of conducting electrode layers. The basic optical data storage device described above may be made in any suitable size such that the device will fit into appropriate data read and write apparatuses, such as, for example, a disk, cassette, optical card, CD or DVD.

5 Optical properties of the optical data storage element **10** as described above can be modified, *e.g.*, by modifying the polymerization of the RMC **14**. Such modification can be performed even after data has been stored in the optical data storage element **10** so long as the final lock has not been carried out. For example, any errors in the stored data may be corrected or new data entered in a post data-write procedure. Applicants believe without being bound to
10 any technical limitations that the stimulus-induced polymerization of the RMC forms a second polymer matrix **18** which can change the refractive index of the optical data storage element in a predictable manner, thus affecting a readable change in the optical data storage element phase contrast.

15 Induction of polymerization of the RMC **14** of an optical data storage element **10** can be achieved by exposing the optical data storage element **10** to a stimulus **16**. In general, a method of inducing polymerization of an optical data storage element **10** having a FPMC **12** and a RMC **14** dispersed therein, comprises:

(a) exposing at least a portion of the optical data storage element **10** to a stimulus **16** whereby the stimulus **16** induces the polymerization of the RMC **14**. If after initial data storage
20 no data needs to be modified, then the exposed portion is the entire optical data storage element **10**. The exposure of the entire optical data storage element **10** with intensity sufficient to induce complete polymerization of the RMC throughout the optical data storage element **10** will lock in the then-existing properties of the optical data storage element **10**.

25 However, if data needs to be modified, then specific areas of the optical data storage element **10** must be re-exposed to the stimulus **16**. Such differential polymerization of the RMC **14** can be achieved via any suitable means of changing the intensity of the stimulus **16** spatially across the optical data storage element **10**, such as, for example, by exposing only a portion of the optical data storage element **10** to the stimulus **16** via a photomask and collimated beam; or alternatively by utilizing a stimulus source capable of variable intensity across the entire
30 area of the optical data storage elements **10**, such that the optical data storage element **10** is subject to a spatially variable stimulus. In one embodiment, the method of implementing the optical data storage element **10** further comprises:

(b) waiting an interval of time to allow macromer diffusion; and

(c) re-exposing a portion of the optical data storage element **10** to the stimulus **16**.

35 This procedure generally will induce the further polymerization of the RMC **14** within the exposed data storage region **20**. Steps (b) and (c) may be repeated any number of times until

1 the data has been stored. The waiting period is important to establish a null point where the volume shrinkage usually seen in photo-induced polymers is overcome by macromer diffusion. At this point, the method may further include the step of exposing the entire optical data storage element **10** to the stimulus **16** to lock-in the desired data.

5 Induction of the polymerization of the RMC in an optical data storage element **10** can also be achieved by:

(a) exposing a first portion of the optical data storage element **10** to a stimulus **16** whereby the stimulus **16** induces the polymerization of the RMC **14**; and

(b) exposing a second portion of the optical data storage element **10** to the stimulus **16**.

10 The first optical data storage portion and the second optical data storage portion represent different regions of the optical data storage element **10** although they may overlap. Optionally, the method may include an interval of time between the exposures of the first optical data storage portion and the second optical data storage portion. In addition, the method may further comprise re-exposing the first optical data storage portion and/or the second optical data storage portion
15 any number of times (with or without an interval of time between exposures) or may further comprise exposing additional portions of the optical data storage element **10** (e.g., a third optical data storage portion, a fourth optical data storage portion, etc.). Once the desired data has been stored, then the method may further include the step of exposing the entire optical data storage element **10** to the stimulus **16** to lock-in the desired data.

20 In general, the location of the one or more exposed portions **20** will vary depending on the amount of data being stored. For example, in one embodiment, the exposed portion **20** of the optical data storage element **10** is the center region of the optical data storage element **10** (e.g., between about 4 mm and about 5 mm in diameter). Alternatively, the one or more exposed optical data storage portions **20** may be along the optical data storage element's **10** outer rim or along a particular meridian. A stimulus **16** for induction of polymerization of the RMC **14** can be any appropriate coherent or incoherent light source.

25 The stored data itself can be in any known high or low resolution format, such as for example where the exposed or stimulated region represents a digital "1" and the non-exposed or non-stimulated region represents a digital "0"; or where the data is stored in an analog or holographic format.
30

Referring to Figure 8a, there is shown a conventional data storage system **100** for an optical recording in an optical storage medium **10**. A source of light **101** provides a beam **102** of collimated incoherent or coherent radiation, such as from a laser for example. The beam **102** is split into a writing beam **103** and a reference beam **104** by beamsplitter **105**. The reference **104** and writing **103** beams interfere at the optical storage medium **10**. A mirror **107** is normally
35 required to redirect one of the beams **103** or **104** to the optical storage medium **10**.

1 A modulation can be placed on the writing beam **103** by modulator **108**. The
modulator **108** may be electrooptic or acoustooptic and may modulate one or more of the phase,
amplitude and polarization of the beam **103**. A computer **109** is typically used to control the
operation of the modulator **108** in a known way so as to encode the beam **103** with desired
5 information which is subsequently stored in the optical storage medium **10**.

The stored information is retrieved from the optical storage medium **10** by the
arrangement shown in Figure 8b. The optical storage medium **10** is illuminated by a light
source **110** with a beam **111**. Typically, the light source **110** has a different wavelength to the
writing light source **101**. Since the reading and writing is occurring at different wavelengths the
10 incident angle of the respective beams with the optical storage medium will be different and set
by the Bragg relation. A reflected beam **112** impinges a detector **113** which supplies signals to,
typically, the computer **109** for analysis to decode the encoded information.

The information stored in the optical storage medium **10** can be erased by irradiation with
a beam **114** from a light source **115** operating at a different wavelength, as depicted in Figure 8c.

15 The procedure described above may be repeated as many times as necessary, such that
after the write beam **104** has entered the desired data, and sufficient time has been allowed for
a change in the optical properties of the optical data storage element **10**, any data aberrations
could be detected by the data read beam **110** and another beam **104**, whose beam characteristics
depend on the second set of data may be applied. This process of write/read/re-write may be
20 continued until the desired data is stored or until the optical data storage element **10** is photo-
locked.

It should be noted that any suitable light source **101**, beam splitter **105**, mirror **107**,
modulator **108**, computer **109**, and detector **113** may be used in the current invention such that
the data can be stored within the optical data storage element **10** and the data read, analyzed and,
25 if necessary, corrected.

For example, the source of light **101** for the write/read/erase cycles could be any suitable
light source, such as, for example, a UV light for high resolution data and IR light for low
resolution data, or a coherent or incoherent visible light source, such as, a frequency doubled
diode laser, a diode laser, or a helium neon laser. The computer and control means may
30 conveniently be embodied in a personal computer. By way of example the approximate power
densities required and achievable are 5-10 mW/cm² at 490 nm for writing, 5 mW/cm² at 780 nm
for reading and 10 mW/cm² at 635 nm for erasing. It will also be appreciated that erasure may
be effected thermally or by an electric field. In these cases the application of the thermal or
electric energy is controlled by the control means. The choice of optical, thermal or electric
35 erasure is dependent on the storage medium of the optical storage means.

1 Although one very general optical storage system is described above with regard to
Figures 8a to 8c, any conventional optical data storage system can be utilized with the current
data storage composition. For example a holographic data storage system **120** using Fourier
hologram recordings could be utilized, as depicted schematically in Figure 9. In such a system,
5 a collimated laser beam **121** is directed through a spatial light modulator (SLM) **122** which
impresses into the beam **121** the desired optical data **123** to be stored in the system. The spatially
modulated output **123** of the SLM **122** is directed towards a positive lens **124**. The SLM **122** is
located at a front focal plane of the lens **124**, while the optical data storage element **10**, is located
at a back focal plane **125**. It is well known that after passing through the lens **124** and arriving
10 at the optical data storage element **10**, the modulated beam **121** generates the spatial Fourier
transform of the original data **123** (see, for example, J. W. Goodman, Introduction to Fourier
Optics, McGraw-Hill, 1968, incorporated herein by reference). Hence, a volume hologram is
formed in the data storage device **10** by the interference of the modulated beam **121** with a
reference laser beam **126** directed orthogonal to the write beam **121** and into the optical data
15 storage element **10**.

 In such a system, once the hologram is created, the original signal can be retrieved by
directing the reference beam **126** into the data storage element **10**. However, the reconstructed
beam **127** initially contains the transformed data not the original data. To render the optical data
in its original form produced by the SLM **122**, the reconstructed beam **127** must be focused by
20 a lens **128**, referred to hereafter as a readout lens. Generally, the readout lens **128** focuses the
beam **127** on the surface of a spatial light detector **129**, most commonly a charge coupled device
(CCD). The resulting image is that of the original data and is consequently recovered by the
detector **129**.

 Although a 4-focal length (4-f) Fourier holography arrangement has traditionally been
25 used for holographic data storage any suitable arrangement may be utilized. As an example, in
a 4-f system, a spatial light modulator **122** is placed at the front focal plane of a first lens **124** and
the optical data storage element **10** is placed at the back focal plane **125** (the Fourier plane) of
the first lens **124**. A second lens **128** is placed after the medium at a distance from the first
lens **124** equal to the sum of the focal lengths of the first **124** and second lens **128**, and a detector
30 array **129** is placed at the back focal plane of the second lens **128**. Each pixel imaged on the
detector array **129** is recorded throughout the optical data storage element **10**. The device **120** is
therefore less susceptible to error than a device which records data only at an image plane.

 As described above, the usual holographic data recording process involves the
interference of two light beams on the data storage composition **10**. It is accomplished by
35 combining an image-bearing light beam and a reference beam in the data storage composition
10. The variation in intensity in the resulting interference pattern causes the complex index of

1 refraction to be modulated throughout the volume of the medium. Figures 10a to 10d
schematically illustrate the operation of a holographic data storage system according to that
shown in Figure 9. During operation two beams, a data beam 121 and a reference beam 126
5 converge at a focal plane 125 creating a static interference pattern corresponding to the data 123,
as shown in Figure 10a. The data storage device 10 containing the data storage composition is
placed in the center of the interference pattern 123, as shown in Figure 10b, such that the
data 123 pattern is imprinted on the data storage composition 10 in the form of a change in
refractivity, absorption, or thickness of the material 123', as shown in Figure 10c. To read the
10 data light from the reference beam 126 is directed at the surface of the composition 10 and the
beam 126 interacts with the pattern 123' to generate a reconstructed data beam 127 which can
then be detected, processed and reported to a user, as shown in Figure 10d. Using such a process
any suitable holograph can be created, such as, for example, a reflective or volume hologram.

Although above we have described the operation of two potential data storage
systems 100 and 120 utilizing the data storage composition 10 of the current invention, it should
15 be understood that any data storage system could be utilized such that sufficient stimulus is
provided to initiate polymerization of the data storage element 10, including the use of a simple
shadow mask, as described in detail in Example 13, below.

The following examples are provided for purposes of exemplifying the invention and
showing its utility only and are not intended to limit the scope of the invention which has been
20 described in broad terms above.

EXAMPLE 1

Suitable optical data storage materials comprising various amounts of (a) poly-
dimethylsiloxane endcapped with diacetoxymethylsilane ("PDMS") (36000 g/mol), (b)
25 dimethylsiloxane-diphenylsiloxane copolymer endcapped with vinyl-dimethyl silane ("DMDPS")
(15,500 g/mol), and (c) a UV-photoinitiator, 2,2-dimethoxy-2-phenylacetophenone ("DMPA")
as shown by Table 1 were made and tested. PDMS is the monomer which forms FPMC, and
DMDPS and DMPA together comprise the RMC.

Appropriate amounts of PMDS (Gelest DMS-D33; 36000 g/mol), DMDPS (Gelest PDV-
30 0325; 3.0-3.5 mole% diphenyl, 15,500 g/mol), and DMPA (Acros; 1.5 wt% with respect to
DMDPS) were weighed together in an aluminum pan, manually mixed at room temperature until
the DMPA dissolved, and degassed under pressure (5 mtorr) for 2-4 minutes to remove air
bubbles. Photosensitive prisms, as shown schematically in Figures 2a to 2d, were fabricated by
pouring the resulting silicone composition into a mold made of three glass slides held together
35 by scotch tape in the form of a prism and sealed at one end with silicone caulk. The prisms are
~5 cm long and the dimensions of the three sides are ~8 mm each. The PDMS in the prisms was

1 moisture cured and stored in the dark at room temperature for a period of 7 days to ensure that
the resulting FPMC was non-tacky, clear, and transparent.

5 **TABLE 1**

	PDMS (wt%)	DMDPS (wt%)	DMPA (wt%) ^a
1	90	10	1.5
2	80	20	1.5
3	75	25	1.5
4	70	30	1.5

10 ^a wt % with respect to DMDPS.

15 The amount of photoinitiator (1.5 wt %) was based on prior experiments with fixed RMC monomer content of 25% in which the photoinitiator content was varied. Maximal refractive index modulation was observed for compositions containing 1.5 wt% and 2 wt % photoinitiator while saturation in refractive index occurred at 5 wt%.

EXAMPLE 2

Synthesis of RMC monomers

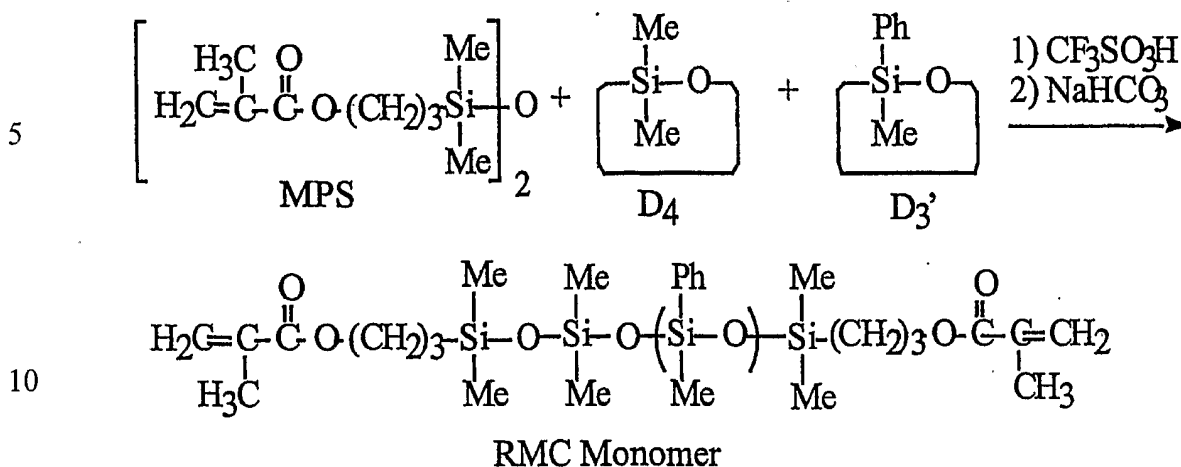
20 As illustrated by Scheme 1, below, commercially available bis-methacryloylpropyltetramethyl- disiloxane ("MPS") dissociates and then ring-opens the commercially available octamethylcyclotetrasiloxane ("D₄") and trimethyltriphenylcyclotrisiloxane ("D₃'") in the presence of triflic acid in a one pot synthesis to form linear RMC monomers. The entire synthesis is described in U.S. Patent No. 4,260,725; Kunzler, J. F., Trends in Polymer Science, **4**: 52-59 (1996); Kunzler et al. J. Appl. Poly. Sci., **55**:
25 611-619 (1995); and Lai et al., J. Poly. Sci. A. Poly. Chem., **33**: 1773-1782 (1995), incorporated herein by reference.

30 Appropriate amounts of MPS, D₄, and D₃' were stirred in a vial for 1.5-2 hours. An appropriate amount of triflic acid was added and the resulting mixture was stirred for another 20 hours at room temperature. The reaction mixture was diluted with hexane, neutralized (the acid) by the addition of sodium bicarbonate, and dried by the addition of anhydrous sodium sulfate. After filtration and rotovaporation of hexane, the RMC monomer was purified by further filtration through an activated carbon column. The RMC monomer was dried at 5 mtorr of pressure between 70-80 °C for 12-18 hours.

35

1

SCHEME 1



The amounts of phenyl, methyl, and endgroup incorporation were calculated from ¹H-NMR spectra that were run in deuterated chloroform without internal standard tetramethylsilane ("TMS"). Illustrative examples of chemical shifts for some of the synthesized RMC monomers follows. A 1000 g/mole RMC monomer containing 5.58 mole% phenyl (made by reacting: 4.85 g (12.5 mmole) of MPS; 1.68 g (4.1 mmole) of D₃'; 5.98 g (20.2 mmole) of D₄; and 108 ml (1.21 mmole) of triflic acid: d = 7.56-7.57 ppm (m, 2H) aromatic, d = 7.32-7.33 ppm (m, 3H) aromatic, d = 6.09 ppm (d, 2H) olefinic, d = 5.53 ppm (d, 2H) olefinic, d = 4.07-4.10 ppm (t, 4H) -O-CH₂CH₂CH₂-, d = 1.93 ppm (s, 6H) methyl of methacrylate, d = 1.65-1.71 ppm (m, 4H) -O-CH₂CH₂CH₂-, d = 0.54-0.58 ppm (m, 4H) -O-CH₂CH₂CH₂-Si, d = 0.29-0.30 ppm (d, 3H), CH₃-Si-Phenyl, d = 0.04-0.08 ppm (s, 50 H) (CH₃)₂Si of the backbone.

A 2000 g/mole RMC monomer containing 5.26 mole% phenyl (made by reacting: 2.32 g (6.0 mmole) of MPS; 1.94 g (4.7 mmole) of D₃'; 7.74 g (26.1 mmole) of D₄; and 136 ml (1.54 mmole) of triflic acid: d = 7.54-7.58 ppm (m, 4H) aromatic, d = 7.32-7.34 ppm (m, 6H) aromatic, d = 6.09 ppm (d, 2H) olefinic, d = 5.53 ppm (d, 2H) olefinic, d = 4.08-4.11 ppm (t, 4H) -O-CH₂CH₂CH₂-, d = 1.94 ppm (s, 6H) methyl of methacrylate, d = 1.67-1.71 ppm (m, 4H) -O-CH₂CH₂CH₂-, d = 0.54-0.59 ppm (m, 4H) -O-CH₂CH₂CH₂-Si, d = 0.29-0.31 ppm (m, 6H), CH₃-Si-Phenyl, d = 0.04-0.09 ppm (s, 112H) (CH₃)₂Si of the backbone.

A 4000 g/mole RMC monomer containing 4.16 mole% phenyl (made by reacting: 1.06 g (2.74 mmole) of MPS; 1.67 g (4.1 mmole) of D₃'; 9.28 g (31.3 mmole) of D₄; and 157 ml (1.77 mmole) of triflic acid: d = 7.57-7.60 ppm (m, 8H) aromatic, d = 7.32-7.34 ppm (m, 12H) aromatic, d = 6.10 ppm (d, 2H) olefinic, d = 5.54 ppm (d, 2H) olefinic, d = 4.08-4.12 ppm (t, 4H) -O-CH₂CH₂CH₂-, d = 1.94 ppm (s, 6H) methyl of methacrylate, d = 1.65-1.74 ppm (m, 4H) -O-CH₂CH₂CH₂-, d = 0.55-0.59 ppm (m, 4H) -O-CH₂CH₂CH₂-Si, d = 0.31 ppm (m, 11H), CH₃-Si-Phenyl, d = 0.07-0.09 ppm (s, 272 H) (CH₃)₂Si of the backbone.

1 Similarly, to synthesize dimethylsiloxane polymer without any methylphenylsiloxane units and endcapped with methacryloxypropyldimethylsilane, the ratio of D₄ to MPS was varied without incorporating D₃.

5 Molecular weights were calculated by ¹H-NMR and by gel permeation chromatography ("GPC"). Absolute molecular weights were obtained by universal calibration method using polystyrene and poly(methyl methacrylate) standards. Table 2 shows the characterization of other RMC monomers synthesized by the triflic acid ring opening polymerization.

10 **TABLE 2**

	Mole % Phenyl	Mole % Methyl	M o l e % Methacrylate	M n (NMR)	Mn (GPC)	n _D
A	6.17	87.5	6.32	1001	946	1.44061
B	3.04	90.8	6.16	985	716	1.43188
C	5.26	92.1	2.62	1906	1880	-----
D	4.16	94.8	1.06	4054	4200	1.42427
E	0	94.17	5.83	987	1020	1.42272
F	0	98.88	1.12	3661	4300	1.40843

15 At 10-40 wt%, these RMC monomers of molecular weights 1000 to 4000 g/mol with 3-6.2 mole % phenyl content are completely miscible, biocompatible, and form optically clear prisms and disks when incorporated in the silicone matrix. RMC monomers with high phenyl content (4-6 mole %) and low molecular weight (1000-4000 g/mol) resulted in increases in refractive index change of 2.5 times and increases in speeds of diffusion of 3.5 to 5.0 times compared to the RMC monomer used in Table 1 (dimethylsiloxane-diphenylsiloxane copolymer endcapped with vinyl dimethyl silane ("DMDPS")) (3-3.5 mole % diphenyl content, 15500 g/mol). These RMC monomers were used to make optical elements comprising: (a) poly-dimethylsiloxane endcapped with diacetoxymethylsilane ("PDMS") (36000 g/mol), (b) dimethylsiloxane methylphenylsiloxane copolymer that is endcapped with a methacryloxypropyldimethylsilane group, and (c) 2,2-dimethoxy-2-phenylacetophenone ("DMPA"). Note that component (a) is the monomer that forms the FPMC and components (b) and (c) comprise the RMC.

30 **EXAMPLE 3**

Fabrication of lense disk data storage elements

35 In another experiment a lense shaped disk mold was designed according to well-accepted standards. See e.g., U.S. Patent Nos. 5,762,836; 5,141,678; and 5,213,825. Briefly, the mold is built around two plano-concave surfaces possessing radii of curvatures of -6.46 mm and/or -12.92 mm, respectively. The resulting lense disks are 6.35 mm in diameter and possess a thickness

1 ranging from 0.64 mm, 0.98 mm, or 1.32 mm depending upon the combination of concave
surfaces used. Using two different radii of curvatures in their three possible combinations and
assuming a nominal refractive index of 1.404, but not limited to, for the disk composition, disks
with pre-irradiation powers of 10.51 D (62.09 D in air), 15.75 D (92.44 in air), and 20.95 D
5 (121.46 D in air) were fabricated.

EXAMPLE 4

Stability of Compositions against Leaching

Three test lense disks were fabricated with 30 and 10 wt% of RMC monomers B and D
10 incorporated in 60 wt% of the PDMS matrix. After moisture curing of PDMS to form the FPMC,
the presence of any free RMC monomer in the aqueous solution was analyzed as follows. Two
out of three disks were irradiated three times for a period of 2 minutes using 340 nm light, while
the third was not irradiated at all. One of the irradiated disks was then locked by exposing the
entire disk matrix to radiation. All three disks were mechanically shaken for 3 days in 1.0 M
15 NaCl solution. The NaCl solutions were then extracted by hexane and analyzed by ¹H-NMR.
No peaks due to the RMC monomer were observed in the NMR spectrum. These results suggest
that the RMC monomers did not leach out of the matrix into the aqueous phase in all three cases.
Earlier studies on a vinyl endcapped silicone RMC monomer showed similar results even after
being stored in 1.0 M NaCl solution for more than one year.

20 Matrix assisted laser desorption ionization time of flight (MALDI-TOF) mass
spectrometry was employed to further study the potential leaching of monomer and matrix into
aqueous solutions. Four lense disks were examined in this study. The first disk was fabricated
with 30 and 10 wt% monomers E and F incorporated in 60 wt% of the PDMS matrix. This disk
was exposed to 2.14 mW/cm² of 325 nm light from a He:Cd laser for four minutes after placing
25 a 0.5 mm width astigmatism mask 23° clockwise from vertical over the lens. The first disk was
then photolocked three

hours after the initial irradiation by exposure to a low pressure Hg lamp for 8 minutes.
The second disk was composed of 30 and 10 wt % monomers B and D incorporated in 60 wt%
of the PDMS matrix. This disk was exposed to 3.43 mW/cm² of 340 nm light from a Xe:Hg arc
30 lamp after placing a 1 mm diameter photomask over the central portion of the disk. The second
disk was not photolocked. The third disk was fabricated with 30 and 10 wt% monomers E and
F incorporated in 60 wt% of the PDMS matrix. This disk was exposed to 2.14 mW/cm² of 325
nm light from a He:Cd laser for four minutes after placing a 1.0 mm diameter photomask over
the central portion of the disk. The third disk was then photolocked three hours after the initial
35 irradiation by exposure to a low pressure Hg lamp for 8 minutes. The fourth disk was fabricated
with 30 and 10 wt% monomers E and F incorporated in 60 wt% of the PDMS matrix. The fourth

1 disk was not irradiated. The four lense disks were placed individually into 5 ml of doubly
distilled water. One ml of dish washing detergent (a surfactant) was added to the solution
containing lens #2. The disks were kept in their respective solutions for 83 days at room
temperature. After this time, the lenses, in their respective solutions, were placed into an oven
5 maintained at 37 °C for 78 days. Each of the aqueous solutions were then extracted three times
using approximately 5 ml of hexane. All hexane extracts from each lens solution were combined,
dried over anhydrous sodium sulfate (Na₂SO₄), and allowed to evaporate to dryness. Each of the
four vials was then extracted with THF, spotted onto a dihydroxy benzoic acid matrix, and
analyzed by MALDI-TOF. For comparison, each of the monomers and PDMS matrix were run
10 in their pure form. Comparison of the four extracted lens samples and the pure components
showed no presence of any of the monomers or matrix indicating that monomer and matrix were
not leaching out of the disks.

EXAMPLE 5

15 Irradiation of Silicone Prisms

Because of the ease of measuring refractive index change (Dn) and percent net refractive
index change ($\%Dn$) of prisms, the inventive formulations were molded into prisms **26** for
irradiation and characterization, as shown in Figures 2a to 2d. As shown in Figure 2a, the
prisms **26** were fabricated by mixing and pouring (a) 90-60 wt% of high M_n PDMS **12** (FPMC),
20 (b) 10-40 wt% of RMC **14** monomers in Table 2, and (c) 0.75 wt% (with respect to the RMC
monomers) of the photoinitiator DMPA into glass molds in the form of prisms 5.0 cm long and
8.0 mm on each side. The silicone composition in the prisms **26** was moisture cured and stored
in the dark at room temperature for a period of 7 days to ensure that the final matrix was non-
tacky, clear, and transparent.

25 Figures 2a to 2d illustrate the prism irradiation procedure. Two of the long sides of each
prism **26** were covered by a black background while the third was covered by a photomask **28**
made of an aluminum plate **30** with rectangular windows **32** (2.5 mm x 10 mm), as shown in
Figure 2b. Each prism **26** was exposed to 3.4 mW/cm² of collimated 340 nm light **16** (peak
absorption of the photoinitiator) from a 1000 W Xe:Hg arc lamp for various time periods.

30 The prisms **26** with the photomask **28** were subject to both (i) continuous irradiation -
one-time exposure for a known time period, and (ii) "staccato" irradiation - three shorter
exposures with long intervals between them. During continuous irradiation, the refractive index
contrast is dependent on the crosslinking density and the mole % phenyl groups, while in the
interrupted irradiation; RMC **14** monomer diffusion and further crosslinking also play an
35 important role. During staccato irradiation, the RMC **14** monomer polymerization depends on
the rate of propagation during each exposure and the extent of interdiffusion of free RMC **14**

1 monomer during the intervals between exposures. Typical values for the diffusion coefficient
of oligomers (similar to the 1000 g/mole RMC 14 monomers used in the practice of the present
invention) in a silicone matrix are on the order of 10^{-6} to 10^{-7} cm²/s. In other words, the inventive
RMC 14 monomers require approximately 2.8 to 28 hours to diffuse 1 mm (roughly the half
5 width of the irradiated bands). After the appropriate exposures, the prisms 26 were irradiated
without the photomask (thus exposing the entire matrix) for 6 minutes using a medium pressure
mercury-arc lamp, as shown in Figure 2d. This polymerized the remaining silicone RMC 14
monomers and thus "locked" the refractive index of the prism in place.

10 EXAMPLE 6

Prism Dose Response Curves

Inventive prisms 26 fabricated from RMC 14 monomers described by Table 2 were
masked and initially exposed for 0.5, 1, 2, 5, and 10 minutes using 3.4 mW/cm² of the 340 nm
line from a 1000 W Xe:Hg arc lamp, as shown schematically in Figures 2a to 2d. The exposed
15 regions 20 of the prisms 26 were marked, the mask 28 detached and the refractive index changes
measured. The refractive index modulation of the prisms 26 was measured by observing the
deflection of a sheet of laser light passed through the prism 26. The difference in deflection of
the beam passing through the exposed 20 and unexposed 22 regions was used to quantify the
refractive index change (Dn) and the percentage change in the refractive index (% Dn).

20 After three hours, the prisms 26 were remasked with the windows 32 overlapping with
the previously exposed regions 20 and irradiated a second time for 0.5, 1, 2, and 5 minutes (total
time thus equaled 1, 2, 4, and 10 minutes respectively). The masks 28 were detached and the
refractive index changes measured. After another three hours, the prisms were exposed a third
time for 0.5, 1, and 2 minutes (total time thus equaled 1.5, 3, and 6 minutes) and the refractive
25 index changes were measured. As expected, the % Dn increased with exposure time for each
prism 26 after each exposure resulting in prototypical dose response curves. Based upon these
results, adequate RMC 14 monomer diffusion appears to occur in about 3 hours for 1000 g/mole
RMC 14 monomer.

All of the RMC monomers (B-F) except for RMC monomer A resulted in optically clear
30 and transparent prisms before and after their respective exposures. For example, the largest %
Dn for RMC monomers B, C, and D at 40 wt% incorporation into 60 wt% FPMC were 0.52%,
0.63% and 0.30% respectively which corresponded to 6 minutes of total exposure (three
exposures of 2 minutes each separated by 3 hour intervals for RMC monomer B and 3 days for
RMC monomers C and D). However, although it produced the largest change in refractive index
35 (0.95%), the prism fabricated from RMC monomer A (also at 40 wt% incorporation into 60 wt%
FPMC and 6 minutes of total exposure - three exposures of 2 minutes each separated by 3 hour

1 intervals) turned somewhat cloudy. Thus, if RMC monomer A were used to fabricate a transparent optical data storage device, then the RMC must include less than 40 wt% of RMC monomer A or the % Dn must be kept below the point where the optical clarity of the material is compromised.

5 A comparison between the continuous and staccato irradiation for RMC A and C in the prisms shows that lower %Dn values occurs in prisms exposed to continuous irradiation as compared to those observed using staccato irradiations. As indicated by these results, the time interval between exposures (which is related to the amount of RMC diffusion from the unexposed to exposed regions) may be exploited to precisely modulate the refractive index of any material made from the inventive polymer compositions.

10 Exposure of the entire, previously irradiated prisms to a medium pressure Hg arc lamp polymerized any remaining free RMC, effectively locking the refractive index contrast. Measurement of the refractive index change before and after photolocking indicated no further modulation in the refractive index.

15

EXAMPLE 7

Optical characterization of data storage elements

16 Talbot interferometry and the Ronchi test, as shown in Figures 3a, 3b and 4 were used to qualitatively and quantitatively measure any optical aberrations (primary spherical, coma, astigmatism, field curvature, and distortion) present in pre- and post-irradiated lense disks **10** as well as quantifying changes in power upon photopolymerization.

20 In Talbot interferometry, the test data storage element **10** is positioned between the two Ronchi rulings with the second grating placed outside the focus of the element and rotated at a known angle, q , with respect to the first grating. Superposition of the autoimage of the first Ronchi ruling ($p_1 = 300$ lines/inch) onto the second grating ($P_2 = 150$ lines/inch) produces Moiré fringes inclined at an angle, a_1 . A second Moiré fringe pattern is constructed by axial displacement of the second Ronchi ruling along the optic axis a known distance, d , from the test element. Displacement of the second grating allows the autoimage of the first Ronchi ruling to increase in magnification causing the observed Moiré fringe pattern to rotate to a new angle, q_2 . Knowledge of Moiré pitch angles permits determination of the focal length of the lens (or inversely its power) through the expression:

$$f = \frac{p_1}{p_2} d \left(\frac{1}{\tan \alpha_2 \sin \theta + \cos \theta} - \frac{1}{\tan \alpha_1 \sin \theta + \cos \theta} \right)^{-1} \quad (1)$$

35

1 To illustrate the applicability of Talbot interferometry to this work, Moiré fringe patterns
of one of the inventive, pre-irradiated data storage elements (60 wt% PDMS, 30 wt% RMC
monomer B, 10 wt% RMC monomer D, and 0.75% DMPA relative to the two RMC monomers)
measured in air is presented in Figures 3a and 3b. Each of the Moiré fringes was fitted with a
5 least squares fitting algorithm specifically designed for the processing of Moiré patterns. The
angle between the two Ronchi rulings was set at 12°, the displacement between the second
Ronchi ruling between the first and second Moiré fringe patterns was 4.92 mm, and the pitch
angles of the Moiré fringes, measured relative to an orthogonal coordinate system defined by the
optic axis of the instrument and crossing the two Ronchi rulings at 90°, were $a_1 = -33.2^\circ \pm 0.30^\circ$
10 and $a_2 = -52.7^\circ \pm 0.40^\circ$. Substitution of these values into the above equation results in a focal
length of 10.71 ± 0.50 mm (power = 93.77 ± 4.6 D).

Optical aberrations of the inventive elements (from either fabrication or from the
stimulus-induced polymerization of the RMC components) were monitored using the "Ronchi
Test" which involves removing the second Ronchi ruling from the Talbot interferometer and
15 observing the magnified autoimage of the first Ronchi ruling after passage through the test
element. The aberrations of the test elements manifest themselves by the geometric distortion
of the fringe system (produced by the Ronchi ruling) when viewed in the image plane.
Knowledge of the distorted image reveals the aberration of the element. In general, the inventive
fabricated elements (both pre and post irradiation treatments) exhibited sharp, parallel, periodic
20 spacing of the interference fringes indicating an absence of the majority of primary-order optical
aberrations, high optical surface quality, homogeneity of n in the bulk, and constant power.
Figure 4 is an illustrative example of a Ronchigram of an inventive, pre-irradiated element that
was fabricated from 60 wt% PDMS, 30 wt% RMC monomer B, 10 wt% RMC monomer D, and
0.75% of DMPA relative to the 2 RMC monomers.

25 The use of a single Ronchi ruling may also be used to measure the degree of convergence
of a refracted wavefront (*i.e.*, the power). In this measurement, the test element is placed in
contact with the first Ronchi ruling, collimated light is brought incident upon the Ronchi ruling,
and the element and the magnified autoimage is projected onto an observation screen.
Magnification of the autoimage enables measurement of the curvature of the refracted wavefront
30 by measuring the spatial frequency of the projected fringe pattern. These statements are
quantified by the following equation:

$$P_v = \frac{1000}{L} \left(1 + \frac{d_s}{d} \right) \quad (2)$$

1 wherein P_v is the power of the element is expressed in diopters, L is the distance from the lens to the observing plane, d_s is the magnified fringe spacing of the first Ronchi ruling, and d is the original grating spacing.

5 EXAMPLE 8

Power changes from photopolymerization of the inventive data storage elements

An inventive element **10** was fabricated as described by Example 3 comprising 60 wt% PDMS **12** ($n_D=1.404$), 30 wt% of RMC monomer B **14** ($n_D=1.4319$), 10 wt % of RMC monomer D **14** ($n_D=1.4243$), and 0.75 wt% of the photoinitiator DMPA relative to the combined weight
10 percents of the two RMC **14** monomers. The data storage element **10** was fitted with a 1 mm diameter photomask **28** and exposed to 3.4 mW/cm² of 340 nm collimated light **16** from a 1000 W Xe:Hg arc lamp for two minutes, as shown in Figure 5a. The irradiated data storage element **10** was then placed in the dark for three hours to permit polymerization and RMC **14** monomer diffusion, as shown in Figure 5b. The data storage element **10** was photolocked by
15 continuously exposing the entire element **10** for six minutes using the aforementioned light conditions, as shown in Figure 5c. Measurement of the Moiré pitch angles followed by substitution into equation 1 resulted in a power of 95.1 ± 2.9 D ($f=10.52 \pm 0.32$ mm) and 104.1 ± 3.6 D ($f=9.61$ mm ± 0.32 mm) for the unirradiated **22** and irradiated **20** zones, respectively.

The magnitude of the power increase was more than what was predicted from the prism
20 experiments where a 0.6% increase in the refractive index was routinely achieved. If a similar increase in the refractive index was achieved in the data storage element, then the expected change in the refractive index would be 1.4144 to 1.4229. Using the new refractive index (1.4229) in the calculation of the optical power (in air) and assuming the dimensions of the element did not change upon photopolymerization, an element power of 96.71 D ($f=10.34$ mm)
25 was calculated. Since this value is less than the observed power of 104.1 ± 3.6 D, the additional increase in power must be from another mechanism.

Further study of the photopolymerized element **10** showed that subsequent RMC **14** monomer diffusion after the initial radiation exposure leads to changes in the radius of curvature of the element **10**, as shown in Figure 5d. The RMC **14** monomer migration from the
30 unirradiated zone **22** into the irradiated zone **20** causes either or both of the anterior **34** and posterior **36** surfaces of the element **10** to swell thus changing the radius of curvature of the element **10**. It has been determined that a 7% decrease in the radius of curvature for both surfaces **34** and **36** is sufficient to explain the observed increase in optical power.

The concomitant change in the radius of curvature was further studied. An identical data
35 storage element **10** described above was fabricated. A Ronchi interferogram of the element **10** is shown in Figure 6a (left interferogram). Using a Talbot interferometer, the focal length of the

1 element **10** was experimentally determined to be 10.52 ± 0.30 mm ($95.1 \text{ D} \pm 2.8 \text{ D}$). The element
10 was then fitted with a 1mm photomask **28** and irradiated with 1.2 mW of 340 collimated light
16 from a 1000 W Xe:Hg arc lamp continuously for 2.5 minutes. Unlike the previous elements,
5 this element **10** was not "locked in" three hours after irradiation. Figure 6b (right interferogram)
is the Ronchi interferogram of the element **10** taken six days after irradiation. The most obvious
feature between the two interference patterns is the dramatic increase in the fringe spacing **38**,
which is indicative of an increase in the refractive power of the element **10**. Measurement of the
fringe spacings **38** indicates an increase of approximately +38 diopters in air ($f \gg 7.5$ mm).
10 Indicating that this mechanism might be utilized in the system of the present invention.

EXAMPLE 9

Photopolymerization studies of non-phenyl-containing data storage elements

Inventive data storage elements **10** using non-phenyl containing RMC monomers **14** were
fabricated to further study the swelling from the formation of the second polymer matrix **18**. An
15 illustrative example of such a data storage element **10** was fabricated from 60 wt% PDMS, 30
wt% RMC monomer E, 10 wt% RMC monomer F, and 0.75% DMPA relative to the two RMC
monomers. The pre-irradiation focal length of the resulting element **10** was $10.76 \text{ mm} \pm 0.25$
mm ($92.94 \pm 2.21 \text{ D}$).

20 In this experiment, the light source **16** was a 325 nm laser line from a He:Cd laser. A 1
mm diameter photomask **28** was placed over the element **10** and exposed to a collimated flux **16**
of 2.14 mW/cm^2 at 325 nm for a period of two minutes. The element **10** was then placed in the
dark for three hours. Experimental measurements indicated that the focal length of the
element **10** changed from $10.76 \text{ mm} \pm 0.25 \text{ mm}$ ($92.94 \text{ D} \pm 2.21 \text{ D}$) to $8.07 \text{ mm} \pm 0.74 \text{ mm}$
($123.92 \text{ D} \pm 10.59 \text{ D}$) or a dioptric change of $+ 30.98 \text{ D} \pm 10.82 \text{ D}$ in air. The amount of
25 irradiation required to induce these changes is only 0.257 J/cm^2 .

EXAMPLE 10

Monitoring for potential optical changes from ambient light

30 The optical power and quality of the inventive data storage elements **10** were monitored
to show that handling under ambient light conditions does not produce any unwanted changes
in element. A 1 mm open diameter photomask was placed over the central region of an inventive
element (containing 60 wt% PDMS, 30 wt% RMC monomer E, 10 wt% RMC monomer F, and
0.75 wt% DMPA relative to the two RMC monomers), exposed to continuous room light for a
period of 96 hours, and the spatial frequency of the Ronchi patterns as well as the Moiré fringe
35 angles were monitored every 24 hours. Using the method of Moiré fringes, the focal length
measured in the air of the optical element immediately after removal from the optical element

1 mold is 10.87 ± 0.23 mm ($92.00 D \pm 1.98 D$) and after 96 hours of exposure to ambient room
light is 10.74 mm ± 0.25 mm ($93.11 D \pm 2.22 D$). Thus, within the experimental uncertainty of
the measurement, it is shown that ambient light does not induce any unwanted change in optical
properties. A comparison of the resulting Ronchi patterns showed no change in spatial frequency
5 or quality of the interference pattern, confirming that exposure to room light does not affect the
power or quality of the inventive data storage elements **10**.

EXAMPLE 11

Effect of the lock in procedure of an irradiated data storage element

10 An inventive data storage element **10** whose optical properties had been modulated by
irradiation was tested to see if the lock-in procedure resulted in further modification of element
optical properties. A data storage element **10** fabricated from 60 wt% PDMS, 30 wt% RMC
monomer E, 10 wt% RMC monomer F, and 0.75% DMPA relative to the two RMC monomers
was irradiated for two minutes with 2.14 mW/cm² of the 325 nm laser line from a He:Cd laser
15 and was exposed for eight minutes to a medium pressure Hg arc lamp. Comparisons of the
Talbot images before and after the lock in procedure showed that the optical power of the
element remained unchanged. The sharp contrast of the interference fringes indicated that the
optical quality of the inventive element also remained unaffected.

To determine if the lock-procedure was complete, the IOL was refitted with a 1 mm
20 diameter photomask and exposed a second time to 2.14 mW/cm² of the 325 nm laser line for two
minutes. As before, no observable change in fringe space or in optical quality of the data storage
element was observed.

EXAMPLE 12

Monitoring for potential data storage element changes from the lock-in

A situation may arise wherein the data storage element does not require post-data storage
modification. In such cases, the element must be locked in so that its characteristic will not be
subject to change. To determine if the lock-in procedure induces undesired changes in the
refractive power of a previously unirradiated data storage element, the inventive data storage
30 element (containing 60 wt% PDMS, 30 wt% RMC monomer E, 10 wt% RMC monomer F, and
0.75 wt% DMPA relative to the two RMC monomers) was subject to three 2 minute irradiations
over its entire area that was separated by a 3 hour interval using 2.14 mW/cm² of the 325 nm
laser line from a He:Cd laser. Ronchigrams and Moiré fringe patterns were taken prior to and
after each subsequent irradiation. The Moiré fringe patterns taken of the inventive data storage
35 element in air immediately after removal from the mold and after the third 2 minute irradiation
indicate a focal length of 10.50 mm ± 0.39 mm ($95.24 D \pm 3.69 D$) and 10.12 mm ± 0.39 mm

1 (93.28 D \pm 3.53D) respectively. These measurements indicate that photolocking a previously
unexposed element does not induce unwanted changes in optical properties. In addition, no
discernable change in fringe spacing or quality of the Ronchi fringes was detected indicating that
the refractive power had not changed due to the lock-in.

5 **EXAMPLE 13**

Phase contrast variation of a composition comprising a refraction modulating composition

To examine the resolution (data density) of the photo-induced refractive materials
composing the data storage elements, the following experiment was performed. Thin films of
10 the photo-induced refractive composition were fabricated by first combining 60 wt% of
diacetoxymethylsilyl endcapped polydimethylsiloxane (PDMS, M_w = 36,000) matrix with 30 wt%
methacryloxypropyldimethylsilyl endcapped polydimethylsiloxane (M_w = 1,000) macromer,
10 wt% methacryloxypropyldimethylsilyl endcapped polydimethylsiloxane (M_w = 4,000)
15 macromer, and 0.75 wt% (relative to the two macromers) of the photoinitiator, 2,2-dimethoxy-2-
phenylacetophenone (DMPA). The composition was mixed thoroughly at room temperature for
5 minutes and degassed at 30-mtorr pressure for 15 minutes to remove any entrapped air. The
material was then placed between two glass slides and allowed to cure at room temperature for
24 hours.

The irradiation was carried out using the 325 nm line of a He:Cd laser. The beam
20 emanating from the laser was focused down on to a 50 μ m pinhole by a 75 mm focusing lens.
A 125 mm lens was placed at a focal distance away from the pinhole to collimate the light
producing a beam diameter of approximately 1.6 mm. Collimation of the beam was insured by
monitoring the tilt angle of the fringes formed from a shearing plate interferometer placed in the
beam.

25 In one experiment, demonstrating the high resolution data storage capabilities of the
inventive material, a 5000 lines/inch (a period of \sim 5 μ m) ruled grating was placed over the top
surface of the sandwiched film and the photo-induced refractive composition was exposed to the
Talbot autoimage of the grating using 6.57 mW/cm² of collimated 325 nm light for 90 seconds.
Figure 11 shows a microscope picture of the film after irradiation through the 5000 lines/inch
30 mask. The magnification of the picture is approximately 125X. The alternating dark and light
stripes running through the picture have a period of approximately 5 μ m as determined by a
calibrated microscope target. Therefore, the photoresponsive materials possess high spatial phase
contrast. In this embodiment the composition of the current invention the exposed or stimulated
region represents a digital "1" and the non-exposed or non-stimulated region represents a digital
35 "0".

1 In a second experiment, shown in Figure 7, two sets of data were stored on a single
photopolymer disk. First a 5000 lines/inch (a period of $\sim 5 \mu\text{m}$) ruled grating was placed over the
top surface of the sandwiched film and then a photomask having the words "CALTECH" and
"CVI" was placed atop that. Then the photo-induced refractive composition was exposed to the
5 Talbot autoimage of the grating and photomask using 6.57 mW/cm^2 of collimated 325 nm light
for 90 seconds. As shown in Figure 7, both the Ronchi rule and the words were inscribed on the
photopolymer disk of the composition according to the present invention, this shows that patterns
of any shape can be utilized to inscribe both high and low resolution data on the same disk of
material simultaneously.

10 In this case, the incident light was orthogonal to the plane of the optical element (slab or
lens) and data, in the form of the Ronchi rule was stored at only a single angle. It will be
understood that data can be stored in the data storage composition **10** of the current invention
more than once and at different angles. Such a multiple storage can be performed by tilting the
slab by a certain angle and exposing it to UV-light through the ronchi ruling. When multiple data
15 is stored by changing the angle, more lines appeared between the 5 micron lines shown in Figures
7 and 11, created by the multiple exposure to light. In addition, by keeping the incident light
orthogonal to the plane of the slab, and rotating the slab by any angle, squares and other three-
dimensional shapes can be formed into the data storage element **10**.

20 The elements of the apparatus and the general features of the components are shown and
described in relatively simplified and generally symbolic manner. Appropriate structural details
and parameters for actual operation are available and known to those skilled in the art with
respect to the conventional aspects of the process.

25 Although specific embodiments are disclosed herein, it is expected that persons skilled
in the art can and will design alternative data storage elements and stat storage systems that are
within the scope of the following claims either literally or under the Doctrine of Equivalents.

30

35

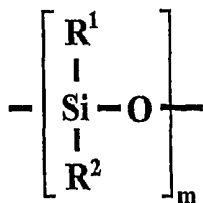
1 CLAIMS

1. A method of recording data comprising:
providing a data storage composition comprising a first polymer matrix and a refraction
modulating composition dispersed therein wherein the refraction modulating composition is
capable of stimulus-induced polymerization; and
stimulating a region of the data storage composition, wherein the stimulated region of the
composition and the non-stimulated region of the composition represent data.
2. The method of recording data as in claim 1 wherein the refraction modulating
composition is capable of photo-induced polymerization.
3. The method of recording data as in claim 1 wherein the first polymer matrix is selected
from the group consisting of poly-carbonates, acrylics, methacrylates, phosphazenes, siloxanes,
vinyls, homopolymers, and copolymers thereof, and side chain and main chain mesogens, and
photochromic and thermochromic moieties, and moieties which undergo a photo-induced
cis/trans isomerization, such as, azo-benzene.
4. The method of recording data as in claim 1 wherein the refraction modulating
composition includes a component selected from the group consisting of an acrylate,
methacrylate, vinyl, siloxane, and phosphazene.
5. The method of recording data as described in claim 1 wherein the first polymer matrix
includes a poly-siloxane.
6. The method of recording data as in claim 1 wherein the first polymer matrix includes a
poly-acrylate.
7. The method of recording data as in claim 1 wherein the refraction modulating
composition comprises a photoinitiator and a monomer of the formula:



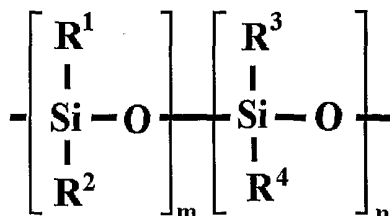
wherein Y is one of either:

1



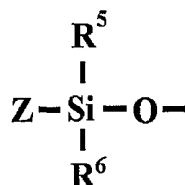
5

or,

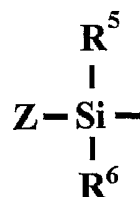


10

X is:



15

and; X¹ is:

20

wherein m and n are each independently an integer and R¹, R², R³, R⁴, R⁵ and R⁶ are each independently selected from the group consisting of hydrogen, alkyl, aryl and heteroaryl; and wherein Z is a photopolymerizable group.

25

30

8. The method of recording data as in claim 7 wherein R¹, R², R³, R⁴, R⁵ and R⁶ are each independently a C₁-C₁₀ alkyl or phenyl, and Z is selected from the group consisting of acrylate, allyloxy, cinnamoyl, methacrylate, stibenyl and vinyl.

35

9. The method of recording data as in claim 7 wherein R¹, R², R³ and R⁵ and R⁶ are selected from the group consisting of methyl, ethyl and propyl and R⁴ is phenyl.

- 1 10. The method of recording data as in claim 7 wherein the monomer is selected from the group consisting of (i) dimethylsiloxane-diphenylsiloxane copolymer endcapped with a vinyl dimethylsilane group, (ii) dimethylsiloxane-methylphenylsiloxane copolymer endcapped with a methacryloxypropyl dimethylsilane group, and (iii) dimethylsiloxane endcapped with a methacryloxypropyl dimethylsilane group, and photoinitiator is 2,2-dimethoxy-2-phenylacetophenone.
- 5
11. The method of recording data as in claim 1 wherein the first polymer matrix is polydimethylsiloxane endcapped with diacetoxymethylsilane.
- 10
12. The method of recording data as in claim 1 wherein the data storage composition further comprises at least one photo-initiator.
13. The method of recording data as in claim 1 wherein the data storage composition is provided in a form selected from the group consisting of a disk, a CD or a DVD.
- 15
14. The method of recording data as in claim 1 wherein the data is stored in a format selected from the group consisting of digital, analog, or three-dimensional image.
- 20
15. The method of recording data as in claim 1 wherein the data is stored as either a reflective or volume hologram.
16. The method of recording data as in claim 1 wherein the stimulus is any wavelength incoherent or coherent source of light.
- 25
17. The method of recording data as in claim 1 wherein the stimulus is a UV light source.
18. The method of recording data as in claim 1 wherein the data storage composition is stable in ambient light.
- 30
19. The method of recording data as in claim 1 wherein the data storage composition is biocompatible.
20. The method of recording data as in claim 1 further comprising the steps of:
waiting an interval of time; and
- 35

1 stimulating or re-stimulating a region of the data storage composition to induce further
polymerization of the refraction modulating composition.

5 21. The method of recording data as in claim 20 further comprising repeating the steps of
waiting and re-stimulating.

22. The method of recording data as in claim 20 wherein the interval of time is determined
by the time required for the diffusion of the refraction modulating composition and the volume
shrinkage of the data composition to reach a null point.

10 23. The method of recording data as in claim 1 further comprising the step of locking-in the
data by stimulating the entire data composition.

24. A composition for data storage comprising:
15 a first polymer matrix and a refraction modulating composition dispersed therein wherein
the refraction modulating composition is capable of stimulus-induced polymerization, and
wherein the stimulated region of the composition and the non-stimulated region of the
composition represent data.

20 25. The composition as in claim 24 wherein the refraction modulating composition is capable
of photo-induced polymerization.

26. The composition as in claim 24 wherein the first polymer matrix is selected from the
group consisting of poly-carbonates, acrylics, methacrylates, phosphazenes, siloxanes, vinyls,
25 homopolymers, and copolymers thereof, and side chain and main chain mesogens, and
photochromic and thermochromic moieties, and moieties which undergo a photo-induced
cis/trans isomerization, such as, azo-benzene.

27. The composition as in claim 24 wherein the refraction modulating composition includes
30 a component selected from the group consisting of an acrylate, methacrylate, vinyl, siloxane, and
phosphazene.

28. The composition as described in claim 24 wherein the first polymer matrix includes a
poly-siloxane.

35 29. The composition as in claim 24 wherein the first polymer matrix includes a poly-acrylate.

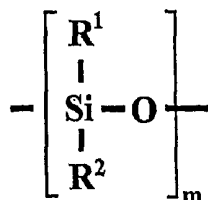
1 30. The method of recording data as in claim 24 wherein the refraction modulating composition comprises a photoinitiator and a monomer of the formula:



5

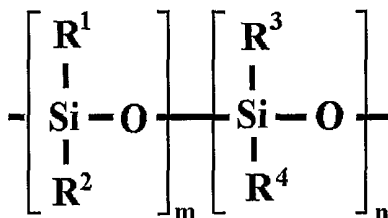
wherein Y is one of either:

10



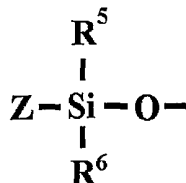
or,

15



X is:

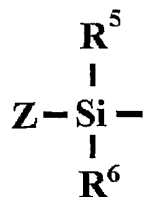
20



25

and; X¹ is:

30



wherein m and n are each independently an integer and R¹, R², R³, R⁴, R⁵ and R⁶ are each independently selected from the group consisting of hydrogen, alkyl, aryl and heteroaryl; and

wherein Z is a photopolymerizable group.

35

- 1 31. The composition as in claim 30 wherein R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are each independently a C_1 - C_{10} alkyl or phenyl, and Z is selected from the group consisting of acrylate, allyloxy, cinnamoyl, methacrylate, stibenyl and vinyl.
- 5 32. The composition as in claim 30 wherein R^1 , R^2 , R^3 and R^5 and R^6 are selected from the group consisting of methyl, ethyl and propyl and R^4 is phenyl.
- 10 33. The composition as in claim 30 wherein the monomer is selected from the group consisting of (i) dimethylsiloxane-diphenylsiloxane copolymer endcapped with a vinyl dimethylsilane group, (ii) dimethylsiloxane-methylphenylsiloxane copolymer endcapped with a methacryloxypropyldimethylsilane group, and (iii) dimethylsiloxane encapped with a methacryloxypropyldimethylsilane group, and photoinitiator is 2,2-dimethoxy-2-phenylacetophenone.
- 15 34. The composition as in claim 24 wherein the first polymer matrix is polydimethylsiloxane endcapped with diacetoxymethylsilane.
- 20 35. The composition as described in claim 24 wherein the first polymer matrix includes a poly-siloxane.
- 25 36. The method of recording data as in claim 24 wherein the data storage composition further comprises at least one photo-initiator.
- 30 37. The method of recording data as in claim 24 wherein the data storage composition is stable in ambient light.
- 35 38. The method of recording data as in claim 24 wherein the data storage composition is biocompatible.
39. A data storage device comprising:
a data storage unit having a data storage composition disposed therein, the data storage composition comprising a first polymer matrix and a refraction modulating composition dispersed therein wherein the refraction modulating composition is capable of stimulus-induced polymerization, and wherein the stimulated region of the composition and the non-stimulated region of the composition represent data;

1 a stimulus generator for generating a stimulus in signal communication with the
composition; and
an analyzer for analyzing the data stored on the data storage composition.

5 40. The data storage device as in claim 39 wherein the refraction modulating composition is
capable of photo-induced polymerization.

41. The data storage device as in claim 39 wherein the first polymer matrix is selected from
the group consisting of poly-carbonates, acrylics, methacrylates, phosphazenes, siloxanes, vinyls,
10 homopolymers, and copolymers thereof, and side chain and main chain mesogens, and
photochromic and thermochromic moieties, and moieties which undergo a photo-induced
cis/trans isomerization, such as, azo-benzene.

42. The data storage device as in claim 39 wherein the refraction modulating composition
15 includes a component selected from the group consisting of an acrylate, methacrylate, vinyl,
siloxane, and phosphazene.

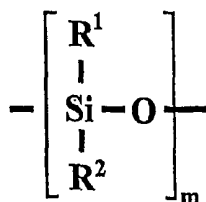
43. The data storage device as described in claim 39 wherein the first polymer matrix includes
20 a poly-siloxane.

44. The method of recording data as in claim 39 wherein the refraction modulating
composition comprises a photoinitiator and a monomer of the formula:



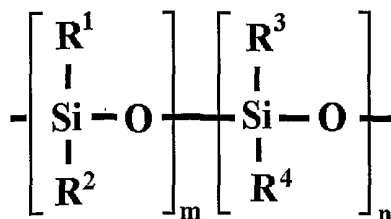
25

wherein Y is one of either:



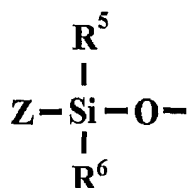
30

or,



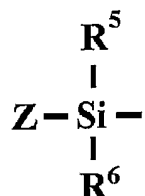
35

1 X is:



5

and; X¹ is:



10

wherein m and n are each independently an integer and R¹, R², R³, R⁴, R⁵ and R⁶ are each independently selected from the group consisting of hydrogen, alkyl, aryl and heteroaryl; and

15

wherein Z is a photopolymerizable group.

25

45. The data storage device as in claim 44 wherein R¹, R², R³, R⁴, R⁵ and R⁶ are each independently a C₁-C₁₀ alkyl or phenyl, and Z is selected from the group consisting of acrylate, allyloxy, cinnamoyl, methacrylate, stibenyl and vinyl.

20

46. The data storage device as in claim 44 wherein R¹, R², R³ and R⁵ and R⁶ are selected from the group consisting of methyl, ethyl and propyl and R⁴ is phenyl.

47. The data storage device as in claim 44 wherein the monomer is selected from the group consisting of (i) dimethylsiloxane-diphenylsiloxane copolymer endcapped with a vinyl dimethylsilane group, (ii) dimethylsiloxane-methylphenylsiloxane copolymer endcapped with a methacryloxypropyl dimethylsilane group, and (iii) dimethylsiloxane endcapped with a methacryloxypropyl dimethylsilane group, and photoinitiator is 2,2-dimethoxy-2-phenylacetophenone.

30

48. The data storage device as in claim 39 wherein the first polymer matrix is polydimethylsiloxane endcapped with diacetoxymethylsilane.

35

49. The data storage device as in claim 39 wherein the data storage composition further comprises at least one photo-initiator.

- 1 50. The data storage device as in claim 39 wherein the data storage unit is selected from the group consisting of a disk, a CD or a DVD.
51. The data storage device as in claim 39 wherein the data storage unit is flexible.
- 5 52. The data storage device as in claim 39 wherein the data is stored in a format selected from the group consisting of digital, analog, or three-dimensional image.
53. The data storage device as in claim 39 wherein the data is stored as either a reflective or
10 volume hologram.
54. The data storage device as in claim 39 wherein the data is stored in either a high or low resolution format.
- 15 55. The data storage device as in claim 39 wherein the data is stored in both a high and low resolution format.
56. The data storage device as in claim 39 wherein the stimulus generator is any wavelength incoherent or coherent source of light.
- 20 57. The data storage device as in claim 39 wherein the stimulus generator is a UV light source.
58. The data storage device as in claim 39 wherein the stimulus generator both writes and
25 reads the data.
59. The data storage device as in claim 58 wherein the stimulus generator utilizes a single wavelength to both write and read the data.
- 30 60. The method of recording data as in claim 39 wherein the data storage composition is stable in ambient light.
61. The method of recording data as in claim 39 wherein the data storage composition is
35 biocompatible.

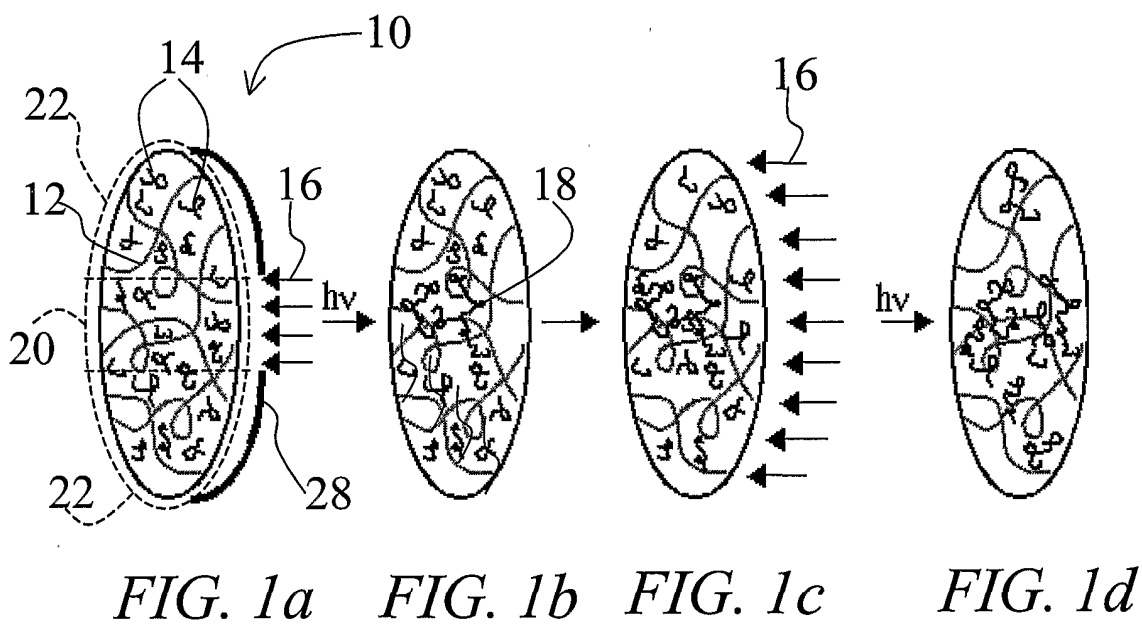
- 1 62. A data storage unit comprising:
 two transparent electrically conducting electrodes; and
 a first polymer matrix and a refraction modulating composition dispersed therebetween
 wherein the refraction modulating composition is capable of stimulus-induced polymerization,
5 wherein the stimulated region of the composition and the non-stimulated region of the
 composition represent data.
63. A data storage unit as in claim 62 wherein the data storage unit is flexible.
- 10 64. A data storage unit comprising:
 a substrate having a tracking layer disposed thereon;
 a transparent protective coating layer; and
 a first polymer matrix and a refraction modulating composition dispersed therebetween
 wherein the refraction modulating composition is capable of stimulus-induced polymerization,
15 wherein the stimulated region of the composition and the non-stimulated region of the
 composition represent data.
65. A data storage unit as in claim 64 wherein the data storage unit is flexible.

20

25

30

35



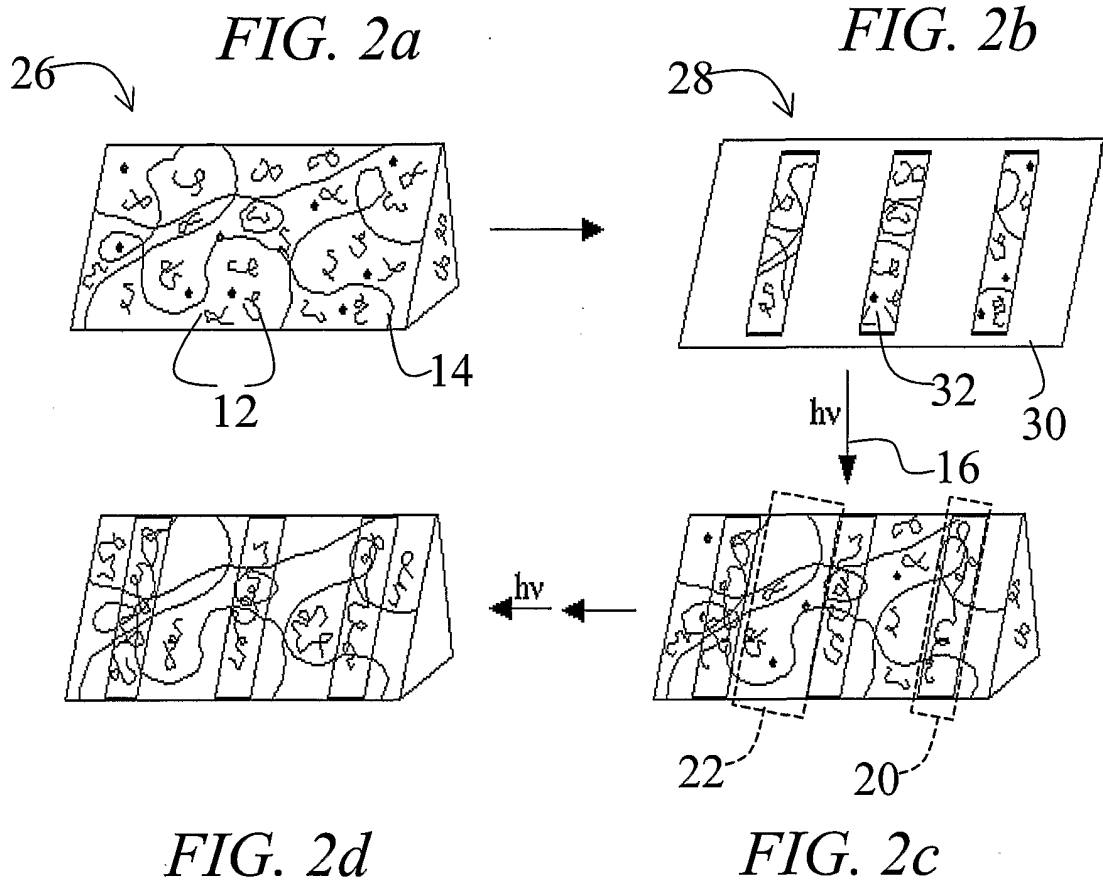


FIG. 3a

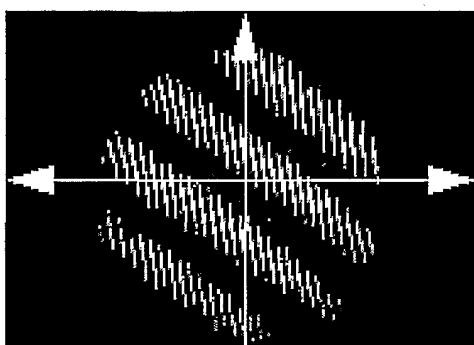


FIG. 3b

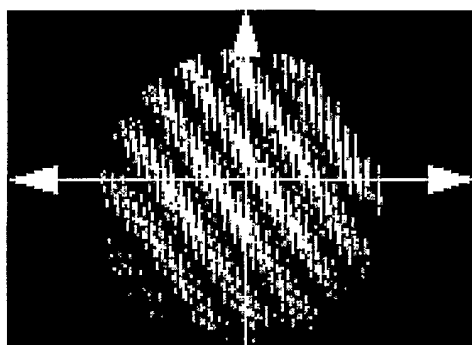
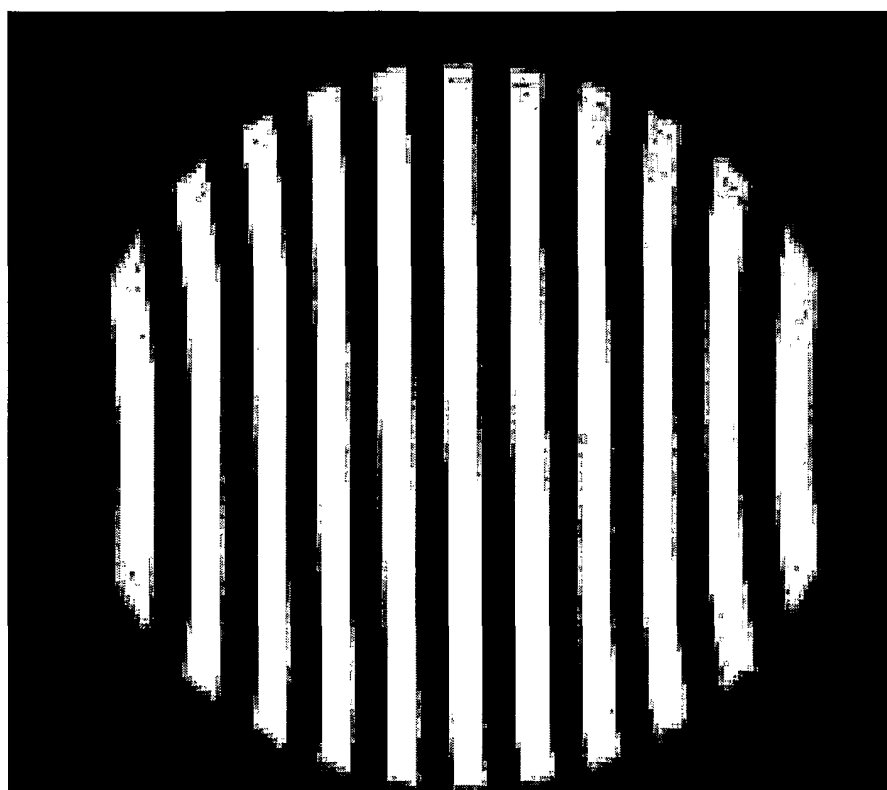


FIG. 4



38

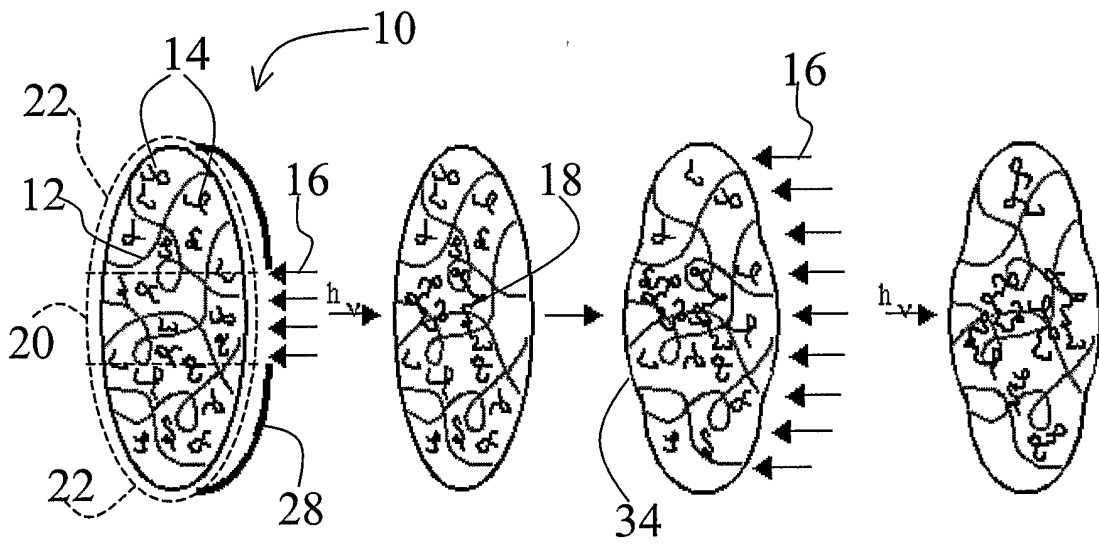


FIG. 5a

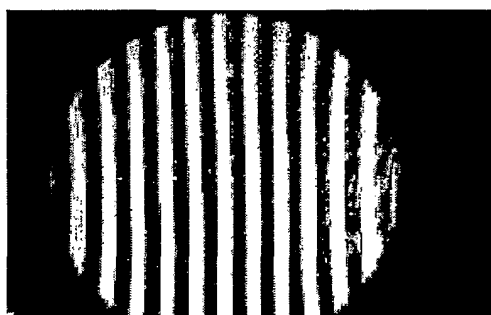
FIG. 5b

FIG. 5c

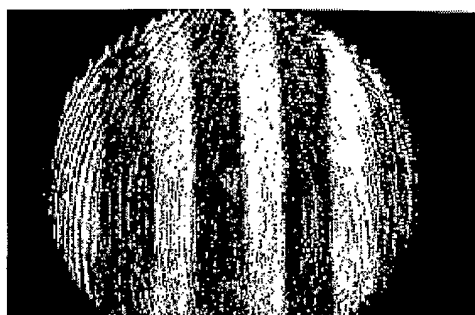
FIG. 5d

FIG. 6a

FIG. 6b



38



38

FIG. 7

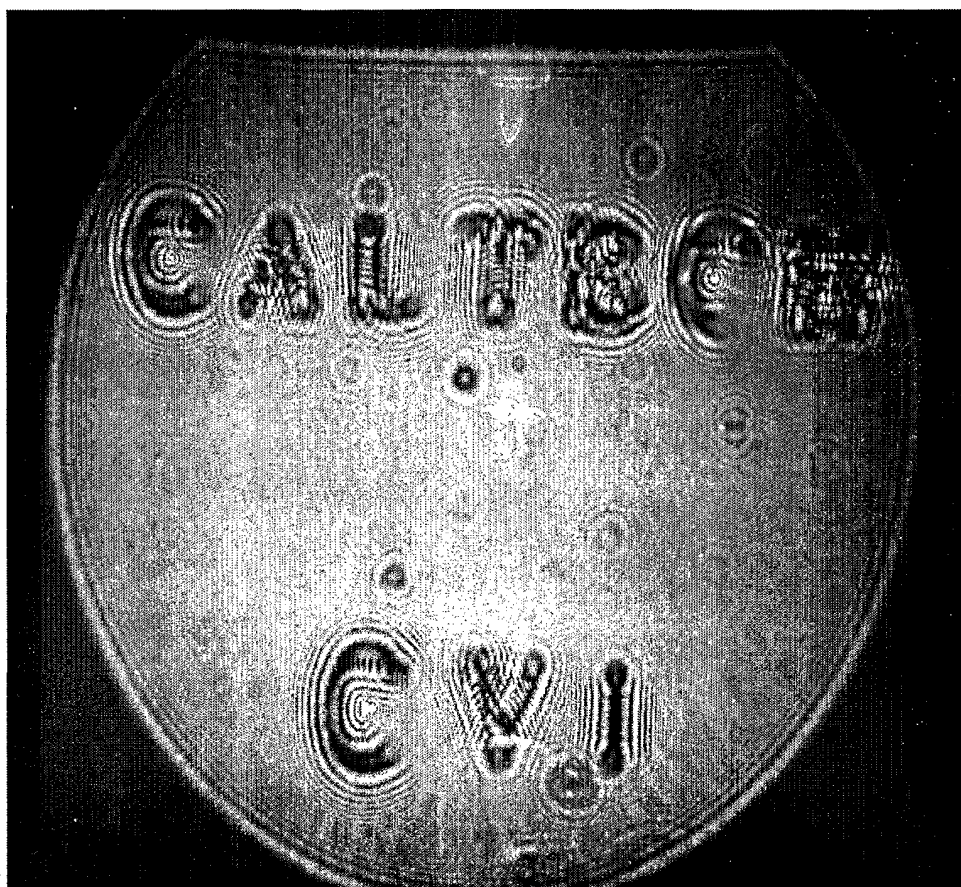


FIG. 8a

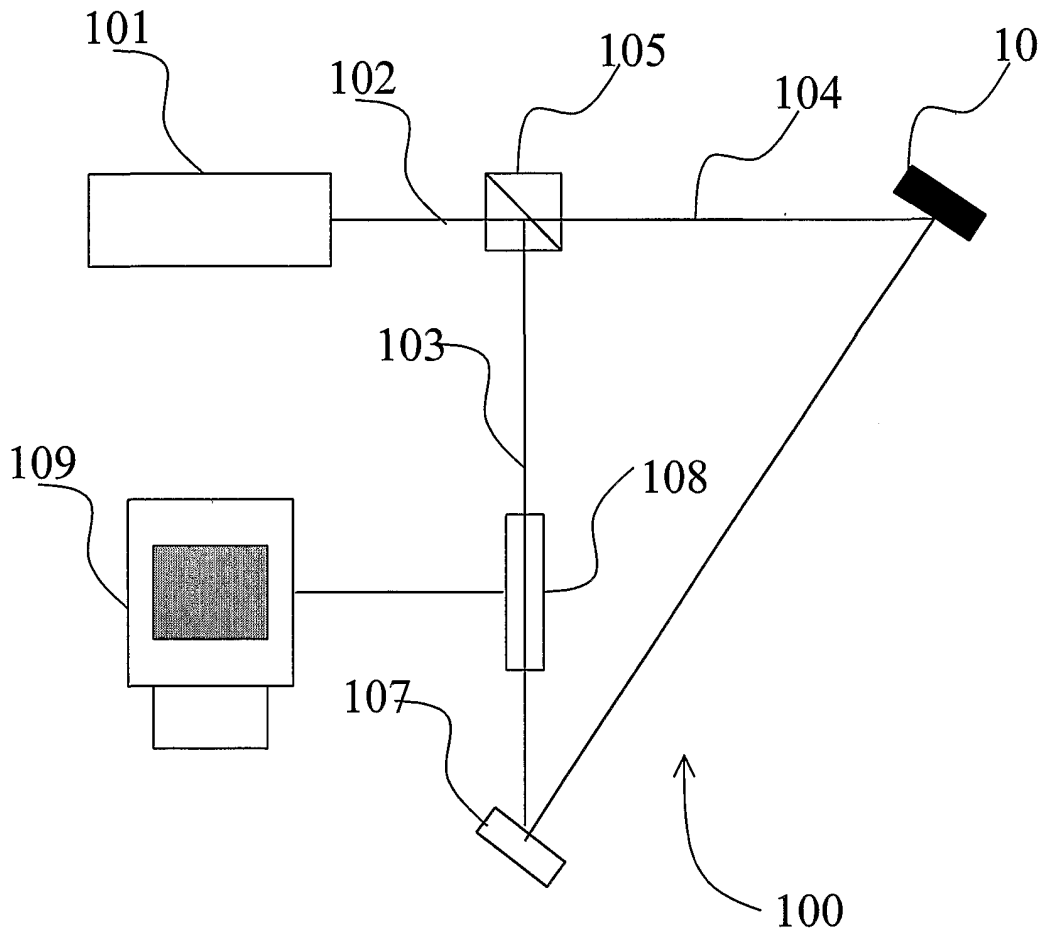


FIG. 8b

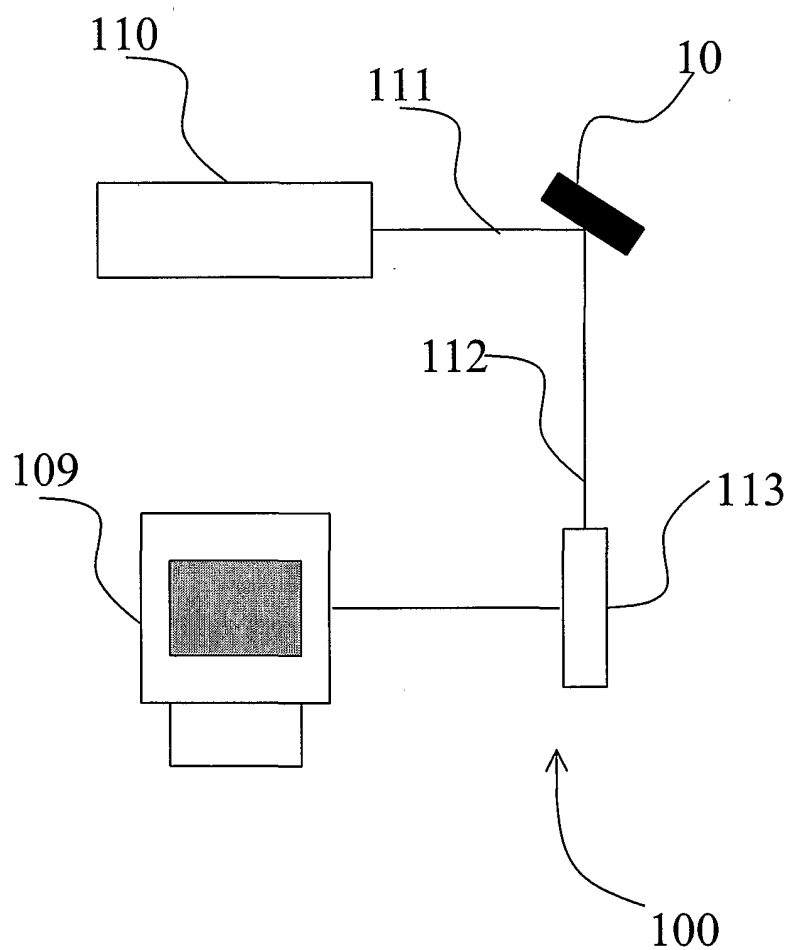


FIG. 8c

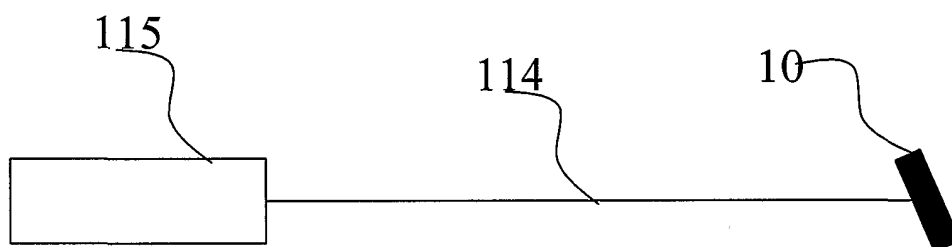


FIG. 9

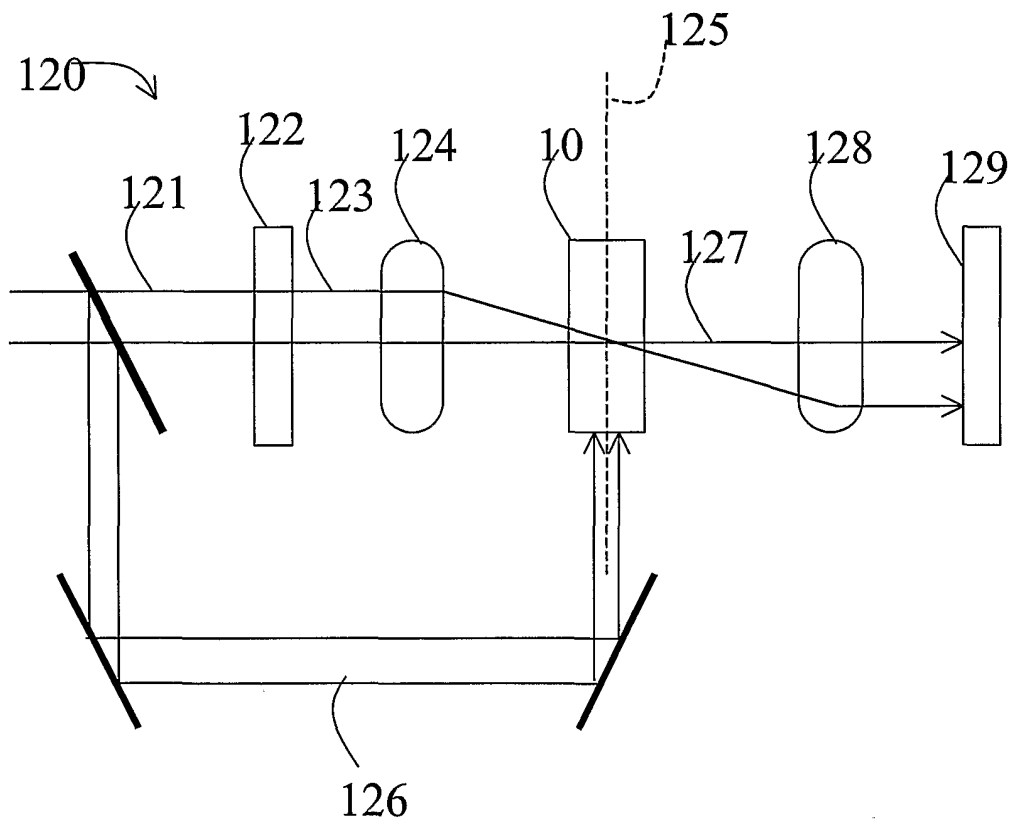


FIG. 10a

FIG. 10b

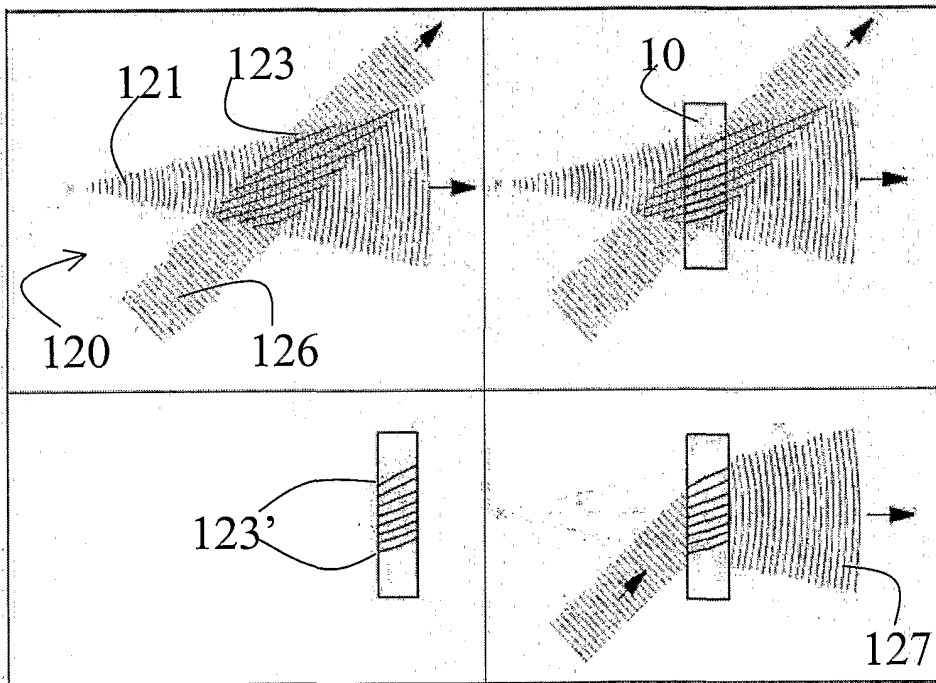


FIG. 10c

FIG. 10d

FIG. 11

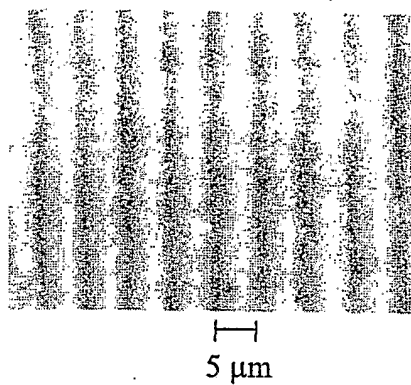


FIG. 12

