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(54) Title: PARTICLE REFLOW ETCHING

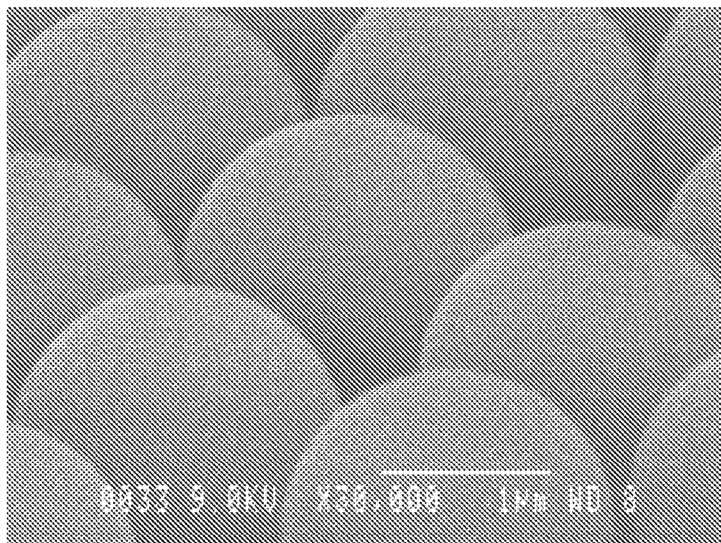

FIG. 8

(57) Abstract: A particle reflow etching method. Coating a dispersed particle solution on a substrate, melting the particles, and etching the substrate. The particles may optionally be etched before melting. Applying a hard mask to a substrate and coating a dispersed particle solution on the hard mask, melting the particles and etching the surface of the hard mask. An article with a substrate and a coating of melted particles. The article may also have a hard mask on the substrate.

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PARTICLE REFLOW ETCHING

Field

The present disclosure relates to etched substrates and processes for making etched
5 substrates.

Summary

In one aspect, the present description relates to a method comprising coating a dispersed particle solution on a substrate, melting the particles, and etching the substrate.
10 In another aspect, the present description relates to a method comprising applying a hard mask to a substrate and coating a dispersed particle solution on the hard mask. The method further comprises melting the particles and etching the surface of the hard mask.

In yet another aspect, the present description relates to an article comprising a substrate and a coating of melted particles. The article may further comprise a hard mask
15 on the substrate.

In yet another aspect, the present description relates to an article comprising a substrate and a coating of particles, shrinking particles, melting particles, and etching the substrate. The article may further comprise a hard mask on the substrate.

20 ## Brief Description of the Drawings

FIG. 1a is a flow chart representing an exemplary reflow etching process.

FIG. 1b is a schematic diagram of an exemplary reflow etching process.

FIG. 2a is a flow chart representing an exemplary reflow etching process.

FIG. 2b is a schematic diagram of an exemplary reflow etching process.

25 FIG. 3 is a flow chart diagramming an exemplary process sequence for melting polystyrene and wet etching.

FIG. 4 is an optical microscope image of polystyrene particles on a substrate.

FIG. 5a is an optical microscope image of melted polystyrene particles on a substrate.

FIG. 5b is a top-view SEM of melted polystyrene particles on a substrate.

30 FIG. 5c is a cross-sectional view SEM of melted polystyrene particles on a substrate.

FIG. 6a is an optical microscope image of a wet etched substrate having random structure with the etch mask still on its surface.

FIG. 6b is an optical microscope image of a wet etched substrate having random structure after removing the etch mask.

FIG. 7 is an SEM image of etched substrate using polystyrene as an etch mask.

FIG. 8 is an SEM image of close packed microspherical PS particles on the top surface of a substrate.

FIG. 9 is an SEM image of etched polystyrene on a substrate.

FIG. 10 is an SEM image of reflowed polystyrene particles on a substrate.

Detailed Description

The present description relates to reflow of particle layers for etching. In particular embodiments, the methods and articles described herein may be particularly useful for preparing roughened surfaces, such as, for light extraction from a semiconductor light emitting diode. The methods and articles described herein are useful, however, for any situation in which a roughened surface is desired.

In one aspect, the present description relates to a method comprising coating a dispersed particle solution on a substrate; melting the particles; and etching the substrate.

The dispersed particle solution may contain any particle materials capable of being melted and serving as an etch mask. For instance, the particles may be silica, low-melting inorganic glass, metal (such as gold, silver, zinc, indium, tin, lead, bismuth, or cadmium), polystyrene, polymethyl(methacrylate) or any thermoplastic polymer, or combinations thereof. Polymeric particles may be, for instance, a polystyrene co-polymer comprising amino groups, a polymethyl(methacrylate) copolymer comprising hydroxyl groups, an epoxy-type polymer, an aldehyde-type polymer, a methyl chloride-type polymer, or a carboxylic acid and/or amino group containing polymer (e.g., an amino acid-type polymer).

One of skill in the art, in light of the present description, will understand that choosing an appropriate particle may be guided, for instance, by considering the appropriate size, adhesive properties, thermal properties, wetting, and etch rates of potential particles. In some embodiments, the particle size is selected to correspond to the depth of desired etched features (for instance when etching is taking place on a photoluminescent or electroluminescent surface, particles should be of comparable size to the wavelength of the light being extracted).

Further, consideration should be given to the adhesion of particles to the substrate. This will be affected by charge on the particles (if any), as well as any surface functionalization (if present) applied to the particles and/or the substrate.

Another consideration in selecting a proper particle and substrate combination is 5 the temperature and time required to reflow the particles, considering whether the temperature and time exposure would damage the substrate. The particles should reflow at a temperature that preferably does not lead to melting or distorting the substrate. Further, the particles should reflow at a temperature that avoids heating the substrate above any temperature that would damage any device structures. This tends to drive the particle 10 materials choice towards thermoplastic polymers, low-melting-temperature glass, or low melting point metals. Exemplary metals include gold, silver, zinc, indium, tin, lead, bismuth, or cadmium. Thermoplastic polymers may also be used, as they allow for reflow without damaging many substrate materials, which cannot tolerate temperatures higher than a 200-300°C. Particle dispersions may be loaded with smaller inorganic particles 15 (e.g., to lower the etch rate).

Also to be considered when selecting a particle-substrate combination is the wetting of the substrate by the melted particle. In some embodiments, for the particles to make good resist layers for wet etching processes they must adhere well to the substrate. This may be influenced by the relative surface energies of the particle and substrate.

20 As a further consideration, one might take into account the relative etch rate of a particle to the substrate via whatever process is being used (that is, etching selectivity). In order to etch deep features, it may be desirable for the reflowed particles to etch much more slowly than the substrate.

Non-uniform features can be obtained by using a distribution of particle sizes, by 25 relying on natural statistical variations in particle spacing (for sparse layers) or by relying on the fact that sparsely-coated (e.g., sub-monolayer) layers tend to show clumping which, after melting, would produce islands of variable size. Using different materials with different etch rates may also produce variable etching profiles, which may or may not be desirable. In the present description, variable depth may be undesirable, where, for 30 instance, light extraction is the intended function of the surface etching (for instance, when etching a photoluminescent device, one may need to control the etch depth to avoid etching into quantum well layers in a photoluminescent device).

The particles may be any size appropriate, taking into account, for instance, dispersion capabilities, surface identity, particle identity, the size of features desired, the etch method to be used, and the like. Particle sizes may range, for instance, from 50nm to 10 μm. In general, the particles may be dispersed in a solvent capable of providing a relatively uniform coating of the particles on a substrate (unless non-uniform features are desired, in which case a different solvent system should be considered). For instance, when the particles are silica, the solvent may be selected from water or an appropriately solvating organic solution. Alternatively, when the particles are polystyrene, the solvent may be selected from an aliphatic alcohol, water, or a combination thereof. Further, when the particles are polymethyl(methacrylate), the solvent may be selected from an aliphatic alcohol, water, or a combination thereof.

For any dispersion described herein, an appropriate surfactant may be added to the dispersion. Surfactants may be selected based upon their dispersing ability in the dispersing medium, the surface properties of the particles, the temperatures to which they will be exposed, the ability of a surfactant to be removed from a surface (by rinsing, etching, or some other method), and the chemical and thermal stability of the surfactant.

Generally, a surfactant can be classified by the presence or absence of formally charged groups (the so-called "head" of the surfactant). A non-ionic surfactant has no charge groups in its head. The head of an ionic surfactant carries a net charge. If the charge is negative, the surfactant is more specifically called anionic; if the charge is positive, it is called cationic. If a surfactant contains a head with two oppositely charged groups, it is termed zwitterionic.

Some commonly encountered surfactants of each type include (a) ionic (i) anionic (e.g., based on sulfate, sulfonate, or coboxylate anions): perfluorooctanoate (so-called PFOA, or PFO), perfluorooctanesulfonate (so-called PFOS), sodium dodecyl sulfate (so-called SDS), ammonium lauryl sulfate (and other alkyl sulfate salts), sodium laureth sulfate (also known as sodium lauryl ether sulfate (SLES)), alkyl benzene sulfonate, and, generally, soaps or fatty acid salts; (ii) cationic (e.g., based on quaternary ammonium cations): cetyl trimethylammonium bromide (so-called CTAB, a.k.a. hexadecyl trimethyl ammonium bromide), and other alkyltrimethylammonium salts, cetylpyridinium chloride (so-called CPC), polyethoxylated tallow amine (so-called POEA), benzalkonium chloride (so-called BAC), and benzethonium chloride (so-called BZT); and (iii) Zwitterionic (also

known as amphoteric): dodecyl betaine, cocamidopropyl betaine, and Coco ampho glycinate; (b) nonionic: alkyl poly(ethylene oxide), alkylphenol poly(ethylene oxide), copolymers of poly(ethylene oxide) and poly(propylene oxide) (commercially known as poloxamers or poloxamines), alkyl polyglucosides (including, for instance, octyl glucoside and decyl maltoside), fatty alcohols (including, for instance, cetyl alcohol and oleyl alcohol), cocamide MEA, cocamide DEA polysorbates (such as those known as Tween 20 and Tween 80. and dodecyl dimethylamine oxide. One skilled in the art will recognize that this is in no way intended to be a comprehensive list of available surfactants but is meant only to provide guidance as to the factors one should consider in selecting an appropriate surfactant for use in dispersions as described herein.

The substrate described herein may be any substrate capable of being etched. For instance, the substrate may be a thermoplastic polymer, a semiconducting material, or a transparent optical glass such as silica or borosilicate, metal such as aluminum, ceramic such as zirconia. When selecting the substrate one should consider that the particles should melt at temperatures below a temperature that negatively affects the substrate (e.g., substrate melting point, decomposition point, deformation temperature, or the like).

When the substrate is a semiconducting material, it may be selected from a group IV semiconductor; a group III-V semiconductor; a group II-VI semiconductor; or any binary, ternary, or quaternary alloys based on a group IV, a group III-V or a group II-VI semiconductor. The substrate may also be a semiconducting material with a solid-state capping layer having a refractive index in the same range as the underlying semiconducting material.

When choosing a combination of particle material and substrate, one may consider such factors as the relative etch rate of the particle material and the substrate. Such relative etch rate may determine the efficacy of a particular particle material as an etch mask for the substrate. In some embodiments, it may be desirable for the particle material to display a relatively high etch rate compared to the substrate.

When the substrate is a group IV semiconductor or a group III-V semiconductor, appropriate particle materials include, for instance, any thermoplastic polymer, or any low-melting inorganic glass or metal. When the substrate is a group II-VI semiconductor, appropriate particle materials include thermoplastic polymers with low melting point such as polystryrene.

FIG. 1a is a flow chart outlining the steps of one embodiment of the methods described herein. These steps are also generally shown in FIG. 1b. First, a dispersed particle solution is coated onto a substrate. Shown in FIG. 1b, particles 120 may, in some embodiments, form a self-assembled mono-layer on substrate 110. Then, particles 120 are optionally shrunk (for instance, using an oxygen plasma to etch particles 120) and melted to give melted particles 130.

The method for optionally etching the particles is selected such that the particles show a much higher reactivity with a chosen reagent than the substrate. For instance, when polystyrene is used as the particle layer and a II-VI semiconducting material is used as the substrate, the polystyrene particles react much more rapidly with the oxygen plasma than does the II-VI semiconducting material. As a result, the particle material is shrunk, but the substrate remains relatively unaffected.

Next, the substrate is etched by wet or dry etching techniques, using melted particles 130 as an etch mask. The result is etched substrate 140. Etched substrate 140 may contain surface features 140a. Such surface features may be useful in any application in which surface roughening is desired. In some embodiments, etched substrate 140 is an outer layer of a light emitting diode device. In such embodiments, etched substrate 140 may provide for higher light extraction than a similar light emitting diode device lacking surface features 140a.

In another embodiment, FIG. 2a is a flow chart outlining the steps of a second embodiment of the methods described herein. These steps are also generally shown in FIG. 2b.

First, a hard mask layer is applied to a substrate. Next, a dispersed particle solution is coated onto the hard mask. Shown in FIG. 2b, particles 220 may, in some embodiments, form a self-assembled mono-layer on hard mask 250. Particles 220 are optionally shrunk (for instance, using an oxygen plasma to etch particles 220) and melted to give melted particles 230.

Then, the surface of hard mask 250 is etched by either dry or wet etching techniques, using melted particles 230 as an etch mask. The result is etched hard mask 260. Finally, substrate 210 is etched by either wet or dry etching techniques, using etched hard mask 260 as an etch mask.

For this embodiment as well, the method for optionally etching the particles is selected such that the particles show a much higher reactivity with a chosen reagent than the hard mask. For instance, when polystyrene is used as the particle layer and a metal material is used as the hard mask, the polystyrene particles react much more rapidly with the oxygen plasma than does the metal material. As a result, the particle material is shrunk, but the hard mask remains relatively unaffected.

The dispersed particle solutions described herein may be coated by any method capable of applying an ordered layer of particle on the surface of either the substrate or the hard coat. In some embodiments, such coating methods provide a mono-layer of particles. Suitable methods include, but are not limited to, dip coating, spin coating, vertical evaporation, convective assembly/deposition, Langmuir-Blodgett assembly, chemical or electrochemical coating, or electrostatically driven coating. When choosing a coating method, one of skill in the art will consider such factors as the size of the substrate (e.g., the surface area); whether the article is a flexible web, in particular if it is to be processed in a roll-to-roll continuous format; the coating uniformity required; and the nature of the solvent used to suspend the particles.

The methods described herein include melting the particles, either when they are on the substrate or on the hard mask. When melting the particles, one of skill in the art will understand that the particles should be heated, for instance, above their melting point, or sufficiently above their glass transition temperature (i.e., Tg) such that they reflow during the allotted process time, but without undesirable decomposition, evaporation, or reaction with the substrate or hard mask. Of course, when melting takes place, for instance, in an oven, care should be taken to choose a particle that can be melted at a temperature that does not damage or decompose the substrate, hard layer, or any other material that is heated at the same time. Techniques potentially useful for melting the particles while imparting a minimum heating to the substrate include infrared radiant heating, flash heating, or exposure to optical radiation (e.g., from a laser) of a wavelength strongly absorbed by the particles but not the substrate.

A number of different dry or wet etching techniques are applicable to the methods described herein. For instance, particles are coated onto a substrate and/or a hard mask. Once coated, the particles may optionally be etched so as to shrink the particles. The etching technique chosen should be one that differentially etches the particles at a much

higher rate than the substrate and/or hard mask. This allows for shrinking of the particles while leaving the substrate and/or hard mask substantially unchanged. Useful techniques for etching the particles include, for instance, dry etching techniques such as plasma etching, reactive ion etching, and reactive ion etching with inductively-coupled plasma. Further useful techniques for etching the particles include, for instance, wet etching techniques such as immersion in well-know acidic or basic etchants suited to the chemical nature of the particles and substrate and/or hard mask.

Once coated on a substrate and/or hard mask, a further etching step can provide surface features in the substrate and/or hard mask. In selecting an appropriate etching technique, one should consider the etch rate ratio between the particles and the substrate or hard mask, the degree of etching anisotropy required (that is, the aspect ratio of the desired structure), and the potential for damage to the substrate during the process. Depending on the identity of the particle and the substrate and/or hard mask, appropriate etching techniques include both dry and wet etching. Dry etching techniques include, for instance, plasma etching, reactive ion etching, reactive ion etching with inductively-coupled plasma. Wet etching techniques include, for instance, immersion in well-know acidic or basic etchants, or solvents

When a hard mask is used, a further etching step includes etching the substrate and removing the hard mask. Depending on the identity of the hard mask and the substrate, appropriate etching techniques include both dry and wet etching. Dry etching techniques include, for instance, plasma etching, reactive ion etching, reactive ion etching with inductively-coupled plasma, or highly anisotropic techniques such as the Bosch process, ion milling, focused ion beam, and other suitable methods known to those skilled in the art. Wet etching techniques include, for instance, immersion in well-know acidic or basic etchants, or solvents.

When the surface of a substrate is etched, surface features are provided. Such surface features can be any appropriate shape for a roughened surface. For instance, when the substrate is a light emitting device, surface features may provide additional light extraction. In such embodiments, conical surface features may be preferable to, say, cylindrical surface features or other surface features having vertical side walls. One method to adjust the wall angle of the features etched into the substrate is to tune the ratio of the etch rates of the melted particles to the substrate. Smaller etch rate ratio tends to

produce walls that deviate more from vertical. Another method is to use controlled isotropic etching (e.g., chemical wet etch) or partial isotropic etching. The etch chemical may remove substrate material laterally, producing walls that deviate from vertical.

Light emitting devices appropriate as substrates include, for instance, electroluminescent devices and photoluminescent devices. When a photoluminescent device is the substrate, suitable substrates include, for instance, group III-V semiconductors and group II-VI semiconductors. Efficiently extracting light from a photoluminescent device is similar to extracting light from a metal-bonded light emitting diode (LED). The majority of the light generated in the emissive layer of an LED is trapped by total internal reflection and waveguiding effects. This is due to the high refractive index of the semiconductor compared to the encapsulant or air. A number of approaches have been demonstrated to improve the light extraction efficiency from high-index LEDs, such as surface roughening by wet or dry etching, photonic crystal patterning, application of particle coatings, or the use of moth-eyed structures. Many of these approaches, however, are limited to specific material systems (e.g., wet chemical roughening of a GaN surface), or are based on expensive fabrication techniques that are not able to be scaled to low cost, high volume manufacturing. In contrast, the methods described herein allow for a flexible means for providing surface roughening that is scalable to low cost and high volume.

General fabrication of micro- or nano-structures using monolayer coatings of particles to serve as etch masks have been reported, but disadvantages to these methods include the relatively high etch rate of the etch mask materials compared to the substrate and the production of columnar post structures (which, as discussed above, may be less efficient for light extraction than conical surface features), and the fact that without melting and fusing to the surface, particles cannot be used at etch masks for wet chemical processes (because the etchant penetrates under the particles).

EXAMPLES

The following examples demonstrate the use of particle reflow etching to produce a roughened substrate surface. In particular embodiments, this roughened substrate surface may, for instance, enhance the light extraction from a high-index semiconductor light emitter such as a light emitting diode (LED).

In the examples that follow, a semiconductor substrate comprised a quantum well wavelength conversion structure fabricated from CdMgZnSe alloys similar to those described in U.S. Provisional Patent Applications 61/075,904, and 61/075,932, the contents of which are incorporated herein in their entirety. In the reported External Quantum Efficiency for these layers, the layers were optically pumped with a blue laser diode to produce light output at longer wavelengths.

Example 1:

The process sequence for using melted polystyrene particles and wet etching a semiconductor substrate to produce light extraction features consisted of:

(1) Coating polystyrene (PS) microspheres on the II-VI color converter layer by spin-on or dip-coating methods or other techniques;

(2) Melting or Reflowing the PS particles; and

(3) Wet etching the color converter using the melted PS as an etch mask.

This process is exemplified by the diagram in Figure 3.

Coating PS particles on a semiconductor substrate

Dispersions of spherical polystyrene (PS) particles with a nominal diameter of 500nm were obtained from the Duke Scientific Corporation (Palo Alto, CA). A 10wt% solution was diluted in H_2O to produce a suspension having 1.5 percent by weight solids content. The 500nm PS particles were coated on a semiconductor substrate (specifically onto a so-called II-VI material comprising ZnMgCdSe epilayers) by dip coating (coating speed: 45mm/min). An optical micrograph of the resulting coating is shown in FIG. 4.

Melting the PS particles

The PS nanoparticles were melted (or reflowed) at 150˚C for 2 minutes. Optical microscope and SEM images of melted PS are shown in FIGs 5a-5c.

Wet etching a semiconductor substrate using PS nano-particle as an etch mask

The semiconductor substrate was isotropically wet chemical etched. The CdMgZnSe layer on which the PS particle mask was melted was immersed into a wet chemical etch solution containing $H_2O:HBr:Br_2$ (120:20:1 by volume) for 15 seconds at room temperature without agitation.

While a relatively short etch time was used in this study, targeting a relatively small etch depth, one of skill in the art will recognize that optimization of the process

could suggest optimal etch conditions for a particular particle-substrate-etching solution combination.

The PS mask was removed using a toluene solution after the wet etching. FIGs. 6a and 6b, respectively, show optical microscope images of the wet etched sample with and without the PS mask.

Quantitative measurements of the sample's photoluminescence (PL) efficiency were made at various stages of the patterning process: before application of the PS particles, after melting of the PS particles, after wet etching, and after removal of the PS mask. Measurements were performed using a radiometrically-calibrated integrating sphere and a 440nm laser diode excitation source. External Quantum Efficiency ("EQE") values derived from the PL measurements are shown in Table 1 below. The EQE of the semiconductor substrate with planar surfaces and no PS coating was about 32.8%. EQE enhancement was achieved with the PS coating alone (~1.3X), and further with the wet etching (~ 1.6X) after removing PS mask.

Table 1

	Semicondutor on Glass	After melt PS	After etch	After cleaning with Toluene
PL	32.8%	43.7%	49%	51.4%

Example 2:

The process sequence for using melted polystyrene particles and wet etching a semiconductor substrate to produce light extraction features consisted of:

(1) coating PS microsphere on II-VI by spin-on or dip-coating method or other techniques;

(2) shrinking and reflowing at least some of the particles; and

(3) wet etching II-VI using melted PS as an etch mask.

This process is exemplified by the diagram in FIG. 1b.

Coating PS nano-particles on a semiconductor substrate

Polystyrene microspheres having an average diameter of about 2000 nm were obtained from VWR Scientific Products (South Plainfield, NJ). The index of refraction of the microspheres was about 1.59. The microspheres were dispersed in H_2O to a 10% solid content by weight. The solution was applied to the top surface of a semiconductor substrate (a so-called II-VI material) using a spin-on coating method at a speed of 200rpm for 20 second and then 5000rpm for 5 second. FIG. 8 is an SEM image of the resulting sample showing close packed microspherical PS particles on the top surface of the semiconductor substrate. The sample was then etched in an oxygen plasma (6 mT, RF power: 80W, and ICP (inductive coupling plasma) power: 1200W) to shrink the PS particles, as shown in FIG. 9.

The EQE of the resulting sample was 17.91%. Hence, the PS particles increased the EQE from 17.91% to 25.91%, a relative increase of about 44.7%. FIG. 9 is an SEM image of the resulting samples. Particles in this figure are cone-like or dome-like. After reactive ion etching RIE shrinking PS size, reflow of the PS particles was carried out at 150°C for 2 minutes. Fig. 10 shows an SEM image of reflowed PS particles. Particles in this figure are cone-like or dome-like with flat bottoms. The EQE of the resulting sample (after reflow) was 28.86%.

Next, the sample was etched with a solution of H_2O:HBr:Br (120:20:1 by volume) for different times (15s, 30s, 45s). Table 2 lists the EQE after different etch times. As can be seen, the EQE is decreased as etch time increases. FIG. 7 is an SEM image of the sample etched for 45s.

Table 2.

Etch time (second)	EQE (%)
15	45.06
30	42.25
45	33.93

We claim:

1. A method comprising:
coating a dispersed particle solution on a substrate;
melting the particles; and
etching the substrate.

2. The method of claim 1, further comprising etching the particles prior to melting the particles.

3. The method of claim 2, wherein etching the particles comprises dry etching.

4. The method of claim 1, wherein the particles are comprised of a thermoplastic polymer.

5. The method of claim 1, wherein the particles are comprised of a metal.

6. The method of claim 1, wherein the particles are comprised of an inorganic glass.

7. The method of claim 4, wherein the particles are selected from a polymer comprising polystyrene, polymethyl(methacrylate), or a combination thereof.

8. The method of claim 1, wherein the substrate is selected from a semiconducting material, a flexible polymer sheet, an inorganic glass, a metal, or a ceramic.

9. The method of claim 8, wherein the semiconducting material is selected from a group IV semiconductor; a group III-V semiconductor; a group II-VI semiconductor; or any binary, ternary, or quaternary alloys based on a group IV, a group III-V or a group II-VI semiconductor.

10. The method of claim 4, wherein the thermoplastic material is selected from polyethyleneterephthalate.

5 11. The method of claim 1, wherein etching comprises wet etching.

12. The method of claim 1, wherein etching comprises dry etching.

13. The method of claim 1 wherein the dispersed particle solution comprises an
10 alcohol solvent, a water solvent, or a combination thereof.

14. The method of claim 1, wherein etching the substrate produces cone-like shaped structures on the substrate.

15 15. The method of claim 1, wherein coating is selected from dip coating, spin coating, vertical evaporation, convective assembly/deposition, Langmuir-Blodgett assembly, chemical or electrochemical coating, or electrostatically driven coating.

16. A method comprising:
20 applying a hard mask to a substrate;
coating a dispersed particle solution on the hard mask;
melting the particles; and
etching the surface of the hard mask.

25 17. The method of claim 16, further comprising etching the substrate, wherein the etched hard mask serves as a resist.

18. The method of claim 16, wherein the hard mask is selected from SiO_2, $S_{i3}N_4$, TiO_2, Al_2O_3, Sb_2O_3, Nb_2O_3, MgO, In_2O_3, AlN, GaN, TiN, indium Tin oxide (ITO),
30 ZrO_2, ZnO, Ta_2O5, HfO_2, silicon oxynitride, Cr, Al, Au. Ti, and Ni.

19. The method of claim 16, further comprising etching the particles prior to melting the particles.

20. The method of claim 19, wherein etching the particles comprises dry
5 etching.

21. The method of claim 16, wherein the particles are selected from polystyrene, polymethyl(methacrylate), silica particles, zinc sulfide particles, titanium dioxide particles, or combinations thereof.
10

22. The method of claim 16, wherein etching the substrate produces cone-like shaped structures on the substrate.

23. An article comprising:
15 a substrate; and
a coating of melted particles.

24. The article of claim 23, wherein the melted particles were exposed to an etching process prior to melting.
20

25. The article of claim 23, wherein the substrate is a semiconductor layer.

26. The article of claim 25 wherein the semiconductor layer is a component of a light emitting diode.
25

27. The article of claim 25 wherein the semiconductor is selected from a group III-V semiconductor and a group II-VI semiconductor.

28. The article of claim 25 wherein the semiconductor layer is a
30 photoluminescent layer capable of absorbing light of a first wavelength and emitting light at a second wavelength distinct from the first wavelength.

29. An article comprising:
a substrate;
a hard mask on the substrate; and
a coating of melted particles.

5

30. The article of claim 29, wherein the melted particles were exposed to an etching process prior to melting.

31. The article of claim 29, wherein the substrate is a semiconductor layer.

10

32. The article of claim 31 wherein the semiconductor layer is a component of a light emitting diode.

33. The article of claim 31 wherein the semiconductor is selected from a group

15 III-V semiconductor and a group II-VI semiconductor.

34. The article of claim 31 wherein the semiconductor layer is a photoluminescent layer capable of absorbing light of a first wavelength and emitting light at a second wavelength distinct from the first wavelength.

20

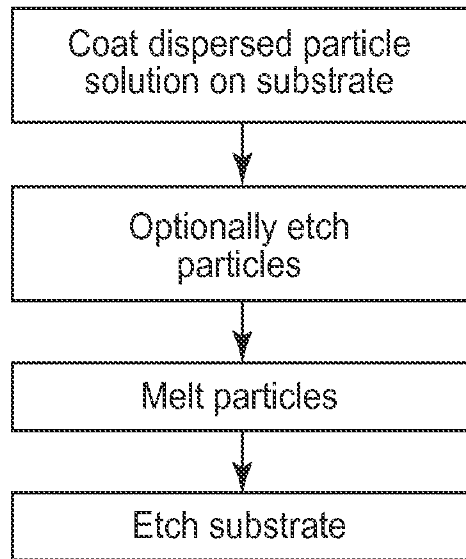

FIG. 1a

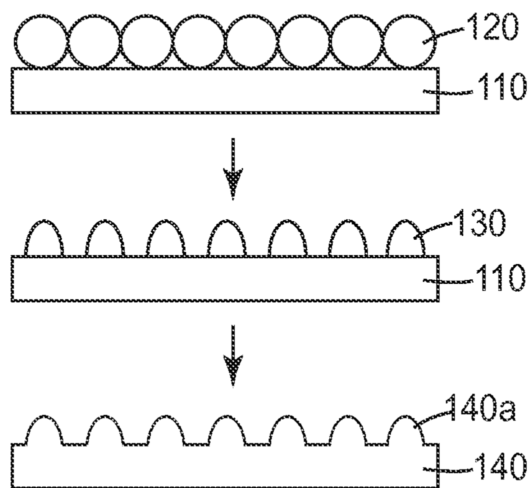

FIG. 1b

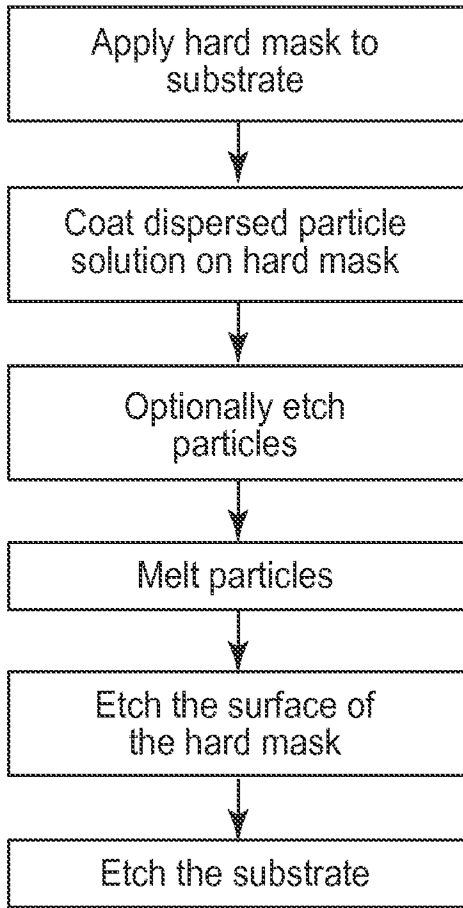

FIG. 2a

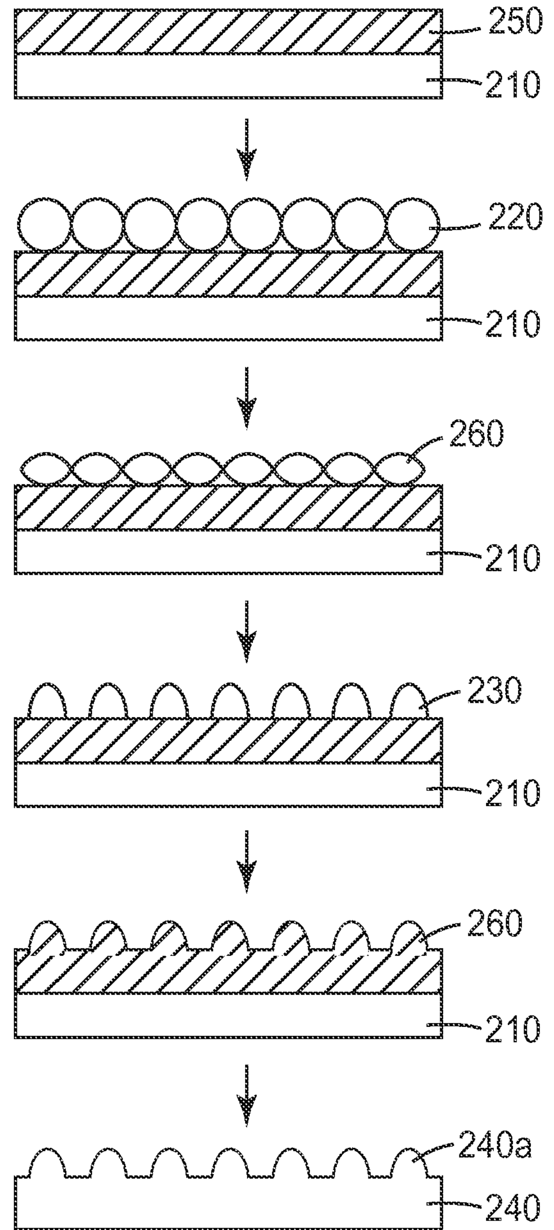

FIG. 2b

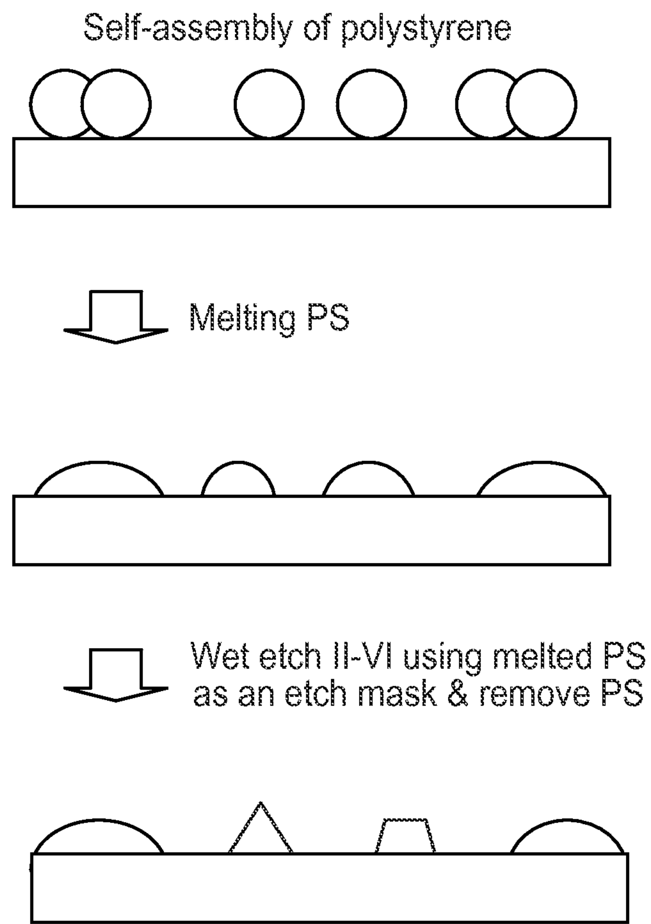

FIG. 3

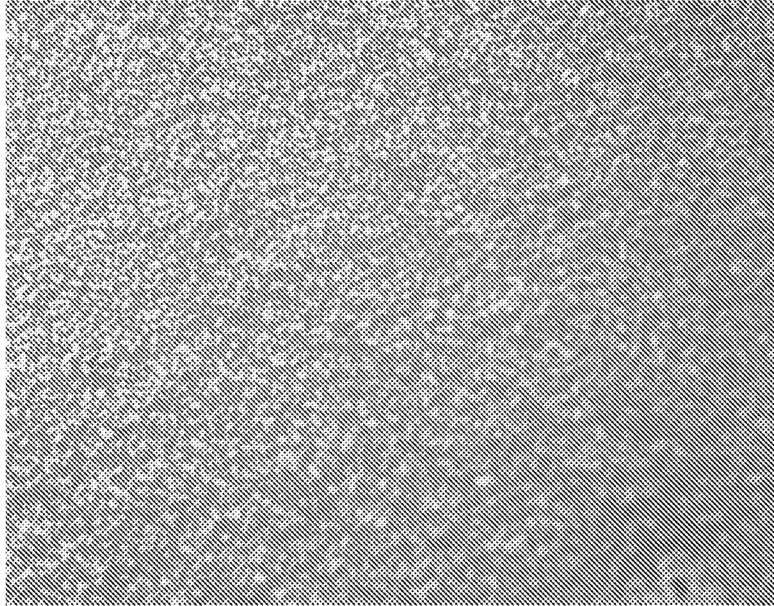

FIG. 4

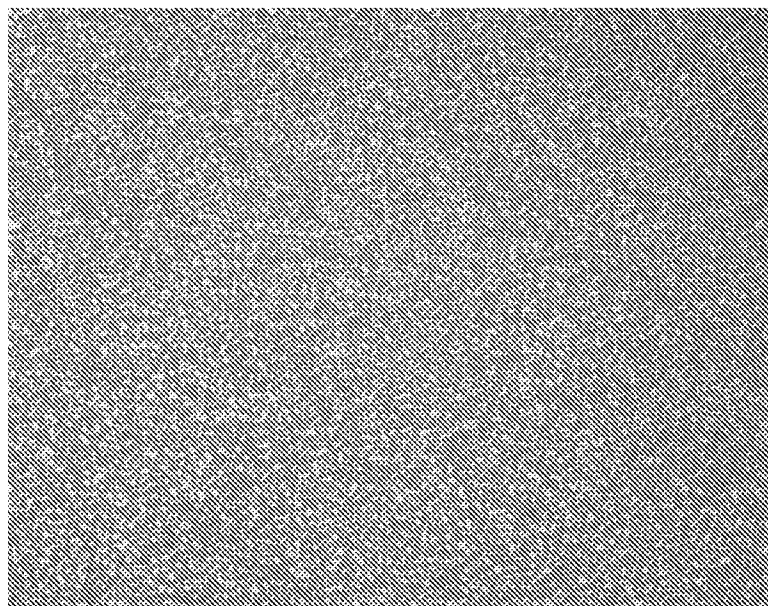

FIG. 5a

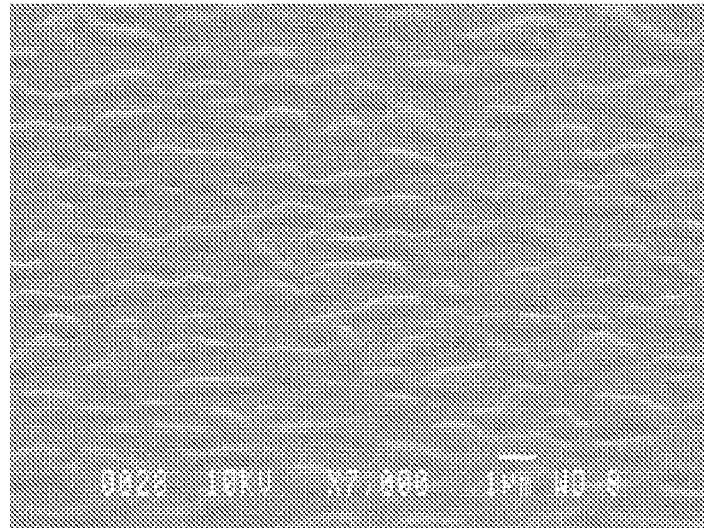

FIG. 5b

FIG. 5c

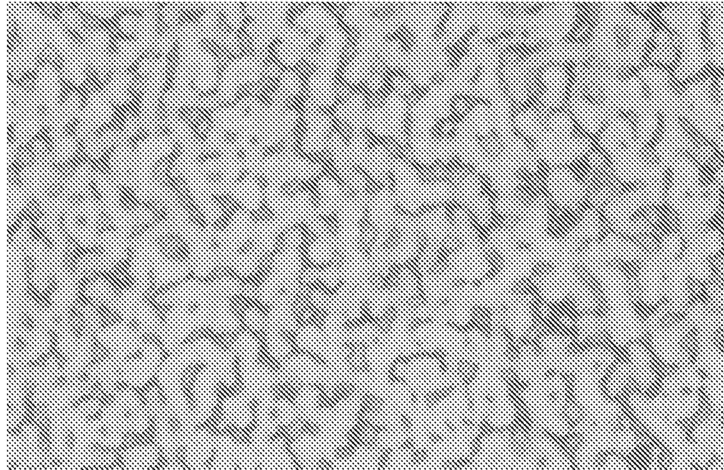

FIG. 6a

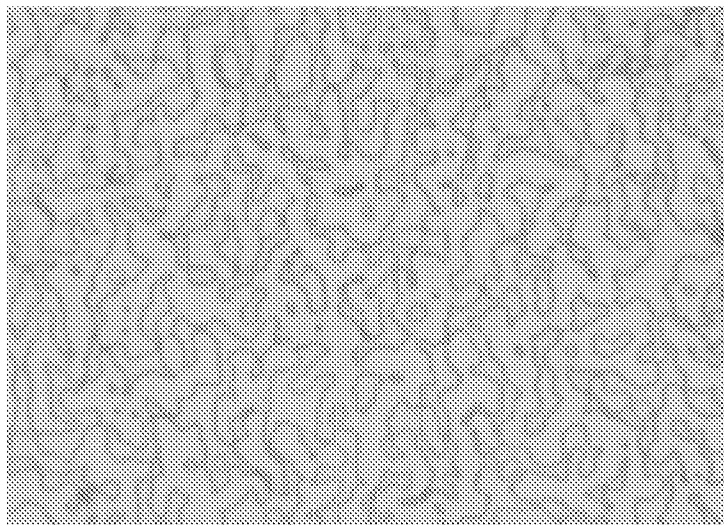

FIG. 6b

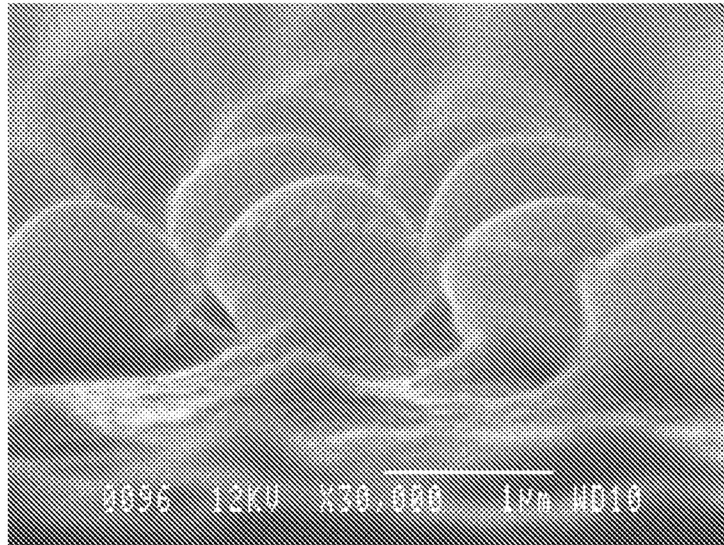

FIG. 7

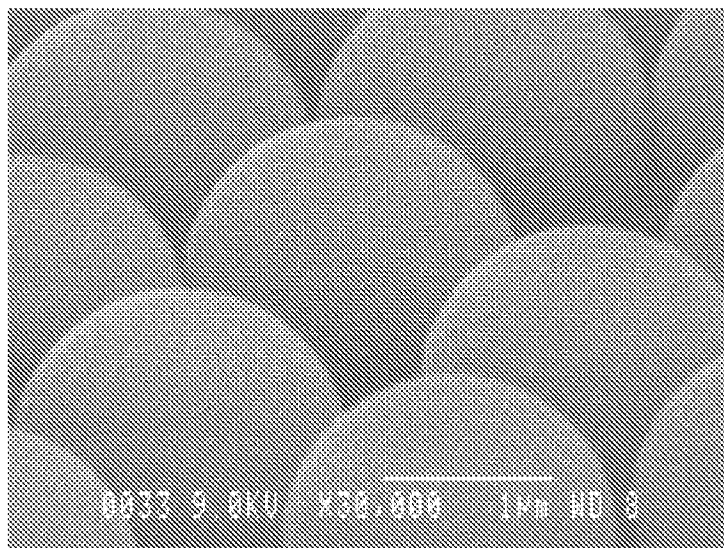

FIG. 8

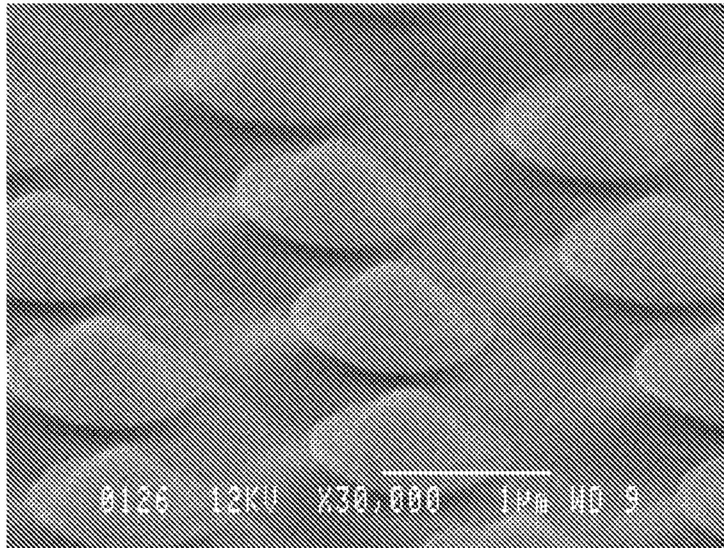

FIG. 9

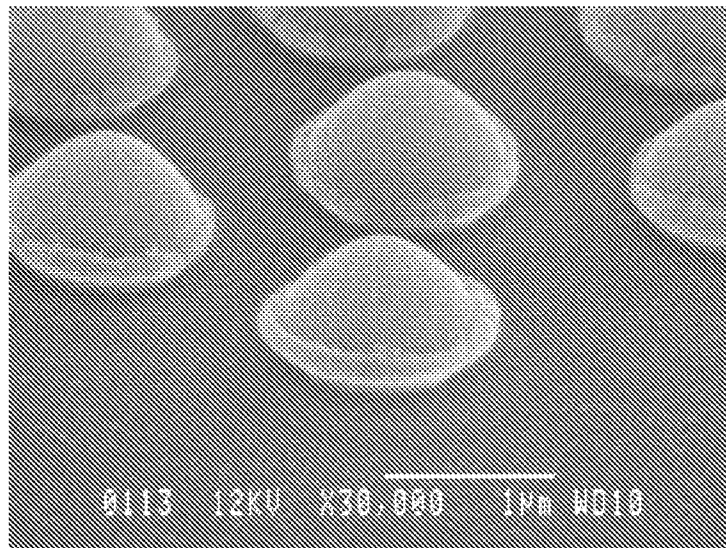

FIG. 10