(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
6 September 2002 (06.09.2002)

PCT

(10) International Publication Number
WO 02/069045 A2

(51) International Patent Classification⁷: **G03F 7/09**

(21) International Application Number: PCT/EP02/01506

(22) International Filing Date: 13 February 2002 (13.02.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
01104284.3 22 February 2001 (22.02.2001) EP

(71) Applicant *(for all designated States except US)*: **INFINEON TECHNOLOGIES SC300 GMBH & CO. KG** [DE/DE]; Königsbrücker Str. 180, 01099 Dresden (DE).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **HORNIG, Steffen** [DE/DE]; Schönburgstr. 62, 01108 Dresden (DE). **GANZ, Dietmar** [DE/DE]; Schonstr. 25, 66806 Ensdorf (DE).

(74) Agent: EPPING, HERMANN & FISCHER; Ridlerstr. 55, 80339 München (DE).

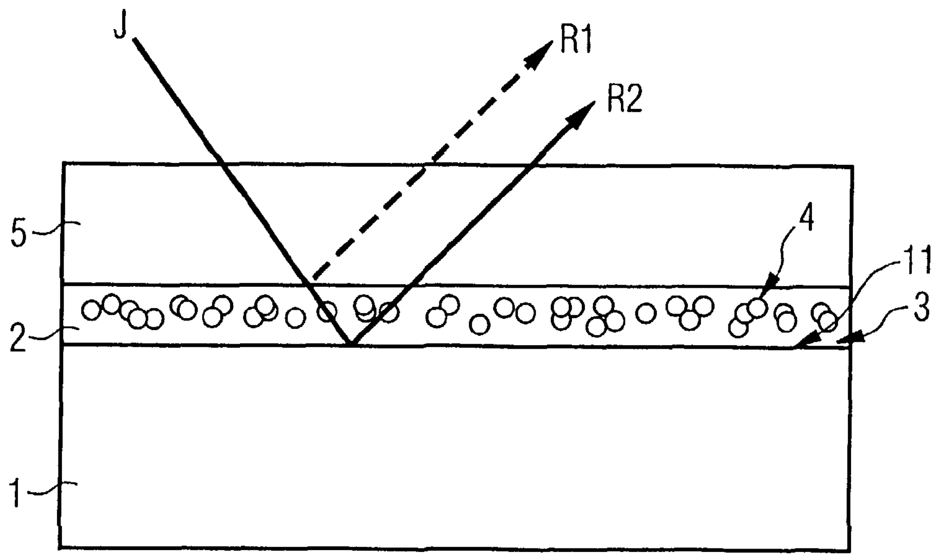
(81) Designated States *(national)*: JP, US.

(84) Designated States *(regional)*: European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

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: ANTI-REFLECTIVE COATING MATERIAL, SEMICONDUCTOR PRODUCT WITH AN ARC LAYER AND METHODS



(57) Abstract: The invention refers to an anti-reflective coating (ARC) layer (2) covering a semiconductor substrate, the ARC layer being made of a matrix substance (3) and of nanocrystalline particles (4) of another material than the matrix substance. According to the invention the nanocrystalline particles (4) are absorbing light via the quantum size effect. Thereby a new kind of ARC layer, in particular absorbing ARC layer, is provided.

WO 02/069045 A2

Description

Anti-reflective coating material, semiconductor product with an ARC layer and methods

The invention refers to an anti-reflective coating (ARC) material for coating a semiconductor product, the anti-reflective coating material being made of a matrix substance and of nanocrystalline particles of another material than the matrix substance.

The invention further refers to a process of producing an anti-reflective coating material by
- providing a matrix material and providing nano-crystalline particles and
- mixing the matrix material and the nano-crystalline particles to form the anti-reflective coating material.

The invention finally refers to a semiconductor product comprising a substrate having a surface with a layer of an anti-reflective coating material arranged on the surface.

In the production of semiconductor products like integrated circuits, wafers are subjected to a lot of process steps like etching, doping and deposition, for instance. Lateral structures of integrated circuits are created by lithography, the semiconductor products being exposed to UV light through a mask pattern. A resist layer on top of the semiconductor product is then etched, thereby either exposed areas or non-exposed areas of the resist layer being removed.

Due to the little depth of the resist layer and the different refractive indexes of the resist layer and the underlying substrate, reflections of exposure light and interferences in the resist layer occur. As a consequence, lateral structures created by lithography tend to deviate from their predefined dimensions.

Diminution of these deviations is achieved by first forming an anti-reflective coating layer, an ARC layer, before forming the resist layer. There are known ARC layers extinguishing reflections by destructive interference of light reflected at the upper and the lower surface of the ARC layer. Other ARC layers reduce reflection by absorption of incoming light.

In another field of the art there are known nanocrystalline particles with particle sizes less than 100 nanometers. They are used for surfaces easy to clean - these surfaces preferably containing fluorine - or for the production of anti-scratch coatings.

It is the object of the present invention to provide a new kind of anti-reflective coating material for coating a semiconductor product or a layer on a semiconductor product to form an ARC layer, particularly an ARC layer of improved properties compared to prior art ARC layers.

This object is achieved by an anti-reflective coating of the kind initially described, the nanocrystalline particles absorbing light via the quantum size effect. According to the invention, light absorption in the ARC layer is achieved by using the quantum size effect. According to this effect, energy levels within the band gap of the ambient material, that is the matrix substance, are created. Electrons at both sides of the band gap may occupy these additional energy levels, thereby absorbing photons of the exposure light. By using this effect for light absorption in nanocrystalline particles of an ARC layer material, a new kind of ARC layer working primarily by absorption is provided. Furthermore, as nanocrystalline particles are too small to cause wave reflections, disturbing reflected beams arising from the ARC layer material are suppressed.

With respect to a semiconductor product the product comprises a substrate having a surface and the anti-reflective coating layer arranged on said surface.

Preferrably, the size of the nanocrystalline particles is less than 100 nanometers in diameter on average. In particular, average particle sizes of less than a quarter of the wavelength of 284, 193, 157 or 127 nm of UV exposure light are preferred.

According to another embodiment of the invention, the material of the particles is chosen corresponding to a predefined wavelength absorbed via the quantum size effect. Depending on the band structure including the band gaps of the matrix substance and the wavelength to be absorbed, the material of the nanocrystalline particles is chosen such that additional energy levels within the band gaps with predefined distance to the valence band or the conduction band are created, the predefined distance corresponding to the wavelength to be absorbed. Preferably, this wavelength is in the UV range.

According to a preferred embodiment, the matrix substance and the material and the concentration of the particles are chosen corresponding to a refractive index of the ARC material. These parameters are chosen such that a refractive index granting maximum light entrance into the ARC layer is achieved. Hence, maximum absorption within the ARC layer by means of the nanocrystalline particles is granted.

According to another embodiment, the material and the concentration of the particles are choosing corresponding to a degree of absorption. The degree of absorption may depend on the thickness of the ARC layer and, of course, on the wavelength to be absorbed.

According to another embodiment, the matrix substance and the size and the concentration of the particles are chosen corresponding to a viscosity value. An ARC layer is formed by coating a semiconductor product, especially a semiconductor wafer or flat panel, with an ARC layer precursor substance. The ARC layer precursor substance consists of the compounds of the ARC layer as well as the solvent allowing to spin on the ARC layer precursor substance onto a rotating semiconductor product. The amount of solvent in the ARC layer is adjusting its viscosity. When material is spun on, the temperature of the material itself is adjusted in order to optimise the spin process, the uniformity of the final layer on the substrate and the material consumption. The adjusted temperature is controlled during the whole spin process in order to guarantee the reliability of the procedure. The spin process is finished when the layer on the substrate has reached a stable condition in terms of drying. Right after the spin process at least one or more heating processes are applied in order to finalise the process of film creation. However, according to this embodiment, further the matrix substance and the size and the concentration of the particles are adjusted in addition with view to a viscosity value.

According to another embodiment, the matrix substance and the material and the concentration of the particles are chosen corresponding to an etch resistance of a dry etch process for etching semiconductor substrates. When a semiconductor product comprising an ARC layer and a resist layer above the ARC layer is etched, etching is proceeded in order to pattern the substrate of the ARC layer in the same way as the pattern mask itself. Precise shaping of three-dimensional structures requires a high etch resistance of the etching mask, that is the resist, and/or of the ARC layer. By carefully choosing the composition of the ARC layer, even this parameter may be controlled.

Preferably, the matrix substance is an organic resin or a silicate. Alternatively, an oxide such as silicon oxide or titanium oxide is preferred.

As to the material of the particles, preferably a metal oxide, a metal sulphide or a perovscite material is chosen. In particular, tin oxide, titanium oxide or cadmium sulphide are preferred. However, there is a lot of other substances with individual band structures leading to appropriate energy levels within the band gap of the matrix substance. Especially oxides and oxide mixtures of metals like Mg, Ca, Ba, Sr, Al, Ga, In, Si, Ge, Ti, Sn, Pb, Sb, Be, Te, Zr, Hf, Nb, Ta, Cr, Mo, W, Mn, Fe, Ru, Co, Rh, Ni, Pd, Zn, Cd, La and of rare earth metals may be taken into account.

Preferably, the ARC layer contains between 3 and 70 % per volume of nanocrystalline particles. The broad range of composition even with respect to the matrix to particle ratio contributes to a most flexible adjustment of the aforementioned parameters.

According to an advanced embodiment of the invention, the ARC layer contains nanocrystalline particles of at least two different materials. Thereby, different ranges of wavelengths may be absorbed. By providing different kinds of particles, a predefined absorption profile may be shaped. Furthermore, fine adjustment of absorption profile may be achieved by choosing particles of a predefined average size.

An anti-reflective coating material according to the invention may be used for covering a semiconductor substrate to be patterned or a layer to be patterned on a semiconductor substrate to form an anti-reflective coating layer dimishing light reflection of exposure light.

With view to the initially mentioned method of producing an anti-reflective coating material the object is solved by using nano-crystalline particles which absorb light via the quantum size effect.

Preferrably the kind of the nano-crystalline particles and/or the concentration of the nano-crystalline particles in the matrix material are chosen such that an anti-reflective coating material having an adjusted refractive index is formed. In particular, by choosing the kind and/or the concentration of the nano-crystalline particles, such a refractive index is adjusted which depends on the refractive index of a resist layer to be applied onto the anti-reflective coating material and/or which depends on the refractive index of a semiconductor substrate to be patterned or of a layer to be patterned on a semiconductor substrate.

With view to the semiconductor product initially described the object of the invention is solved by providing an anti-reflective coating material on the surface which is an anti-reflective coating material according to the invention, that is by providing an anti-reflective coating material which absorbs light via the quantum size effect.

Preferably the semiconductor product comprises a resist layer on top of the ARC layer, the resist layer preferably being made of an organic material.

When the kind and/or the concentration of the nano-crystalline particles are chosen to adjust such a refractive index of the anti-reflective coating material which depends on the refractive index of a resist layer to be applied onto the anti-reflective coating material, light reflection on top of the ARC material layer is reduced. Hence, at the intermediate surface between the resist layer and the ARC material layer, most part of incoming light is entering the ARC material layer material and is being absorbed by the nanocrystalline particles.

Hereinbelow the invention is described with reference to the accompanying figures.

Figure 1 illustrates a semiconductor product according to prior art.

Figure 2 illustrates a semiconductor product according to the present invention.

Figure 3 illustrates a method of forming and applying an anti-reflective coating material according to the invention.

In figure 1, an incoming light beam I entering the resist layer 5 is partially reflected at the intermediate surface between the resist layer and the ARC layer 2 below, the reflected beam being denoted as R1. The remaining intensity enters the ARC layer and is reflected at the intermediate surface 11 between the ARC layer 2 and the substrate 1, the resulting reflected beam R2 extinguishing the other beam R1 at least in part via destructive interference.

In case of absorbing ARC layers, the refractive index of the ARC layer 2 is adjusted to be similar to the refractive index of the resist layer 5, thereby producing maximum transmission of beam I into layer 2 and absorbing beam I within the ARC layer material. The present invention predominantly refers to the absorbing kind of ARC layers, however, it applies also to destructive interference ARC layers as with view to the three refractive indexes of resist 5, ARC layer 2 and substrate 1 an intensity variation of reflected beam R2 may be useful. The reflected beam R1 is drawn in dashed lines as its intensity is rather low in case of absorbing ARC layers.

Whereas prior art ARC layer material is homogeneous, according to the present invention illustrated in figure 2, the ARC layer 2 comprises a matrix substance 3 embedding nanocrystalline particles 4 causing absorption of incoming light via the quantum size effect. Preferably two or more kinds of particles 4a, 4b are provided.

By exploiting this mechanism in ARC layer 2, the reflected beam 2 is absorbed. The absorption profile can be shaped by providing different kinds or sizes of nanocrystalline particles, these and other composition parameters allowing an adjustment of further physical properties of the ARC layer itself.

The production of the ARC layer material compounds is produced in well-known manner. Nanocrystalline particles are extracted by chemical hydrolysis condensation; the matrix substance is produced by a sole gel process. According to the invention, the matrix substance and the nanocrystalline particles are mixed and other chemical substances like solvents or surface-active agents for better adhesion to the substrate are added. The ARC layer material composition is then spun onto the substrate and then heated up to a temperature not above 200° C in order not to crack polymer hydrocarbon chains of the matrix substance. During the heating, a certain amount of the solvent is removed and matrix substance molecules are interconnected with one another, thereby forming a network safely embedding the nanocrystalline particles.

It will be familiar to a skilled person to chose kinds and quantities of the matrix substance and of the nanocrystalline particles in order to appropriately tune physical properties like refractive index, absorption profile, viscosity and etch resistance of the ARC layer.

Accoding to figure 3 an anti-reflective coating material is produced by first providing a matrix material 3, providing nano-crystalline particles 4 and mixing the matrix material 3 and the nano-crystalline particles 4 with one another to form the anti-reflective coating material 2. According to the invention nano-crystalline particles 4 absorbing light via the quantum size effect are used. The anti-reflective coating material 2 is then applied to a semiconductor substrate 1 to be patterned or to a layer 1 to be patterned on a semiconductor substrate thereby forming an anti-reflective coating layer 2. The material of the nano-crystalline particles 4 and their concentration in the matrix material 3 are chosen such that an anti-reflective coating material 2 having an adjusted refractive index ε1 is formed. Preferrably, by choosing the kind and/or the concentration of the nano-crystalline particles 4, such a refractive index ε1 of the anti-reflective coating layer 2 is adjusted which depends on the refractive index ε0 of a resist layer to be applied onto the anti-reflective coating material 2. The refractive index ε1 may further depend on the refractive index ε2 of a semiconductor substrate 1 to be patterned or of a layer 1 to be patterned on a semiconductor substrate.

Claims

1. Anti-reflective coating (ARC) material (2) for coating a semiconductor product,
the anti-reflective coating material (2) being made of a matrix substance (3) and of nanocrystalline particles (4) of another material than the matrix substance,
characterised in that
the nanocrystalline particles (4) are absorbing light via the quantum size effect.

2. Anti-reflective coating material according to claim 1,
characterised in that
the size of the nanocrystalline particles (4) is less than 100 nanometers in diameter on average.

3. Anti-reflective coating material according to claim 2,
characterised in that
the size of the nanocrystalline particles (4) is less than a quarter of the wavelength of 248, 193, 157 or 127 nm of UV exposure light.

4. Anti-reflective coating material according to one of claims 1 to 3,
characterised in that
the material of the particles (4) is chosen corresponding to a wavelength absorbed via the quantum size effect, the wavelength preferrably being in the UV range.

5. Anti-reflective coating material according to one of claims 1 to 4,
characterised in that
the matrix substance (3) and the material and the concentration of the particles (4) are chosen corresponding to a refractive index (ε1) of the ARC material (2).

6. Anti-reflective coating material according to one of claims 1 to 5,
characterised in that
the material and the concentration of the particles are chosen corresponding to a degree of absorption.

7. Anti-reflective coating material according to one of claims 1 to 6,
characterised in that
the matrix substance (3) and the size and the concentration of the particles (4) are chosen corresponding to a viscosity value.

8. Anti-reflective coating material according to one of claims 1 to 7,
characterised in that
the matrix substance (3) and the material and the concentration of the particles (4) are chosen corresponding to an etch resistance of a dry etch process for etching semiconductor substrates.

9. Anti-reflective coating material according to one of claims 1 to 8,
characterised in that
the matrix substance (3) is an organic resin, a silicate or an oxide like a silicon oxide or like titanium oxide.

10. Anti-reflective coating material according to one of claims 1 to 9,
characterised in that
the material of the particles (4) is a metal oxide, a metal sulphide or a perovscite material.

11. Anti-reflective coating material according to one of claims 1 to 10,
characterised in that

the material of the particles contains tin oxide, titanium oxide or cadmium sulphide.

12. Anti-reflective coating material according to one of claims 1 to 11,
characterised in that
the ARC layer contains between 3 and 70 % per volume of nano-crystalline particles (4).

13. Anti-reflective coating material according to one of claims 1 to 12,
characterised in that
the ARC layer contains nanocrystalline particles (4) of at least two different materials (4a, 4b).

14. Method of covering a semiconductor substrate (1) to be patterned or a layer (1) to be patterned on a semiconductor substrate with an anti-reflective coating material (2) according to one of claims 1 to 13 to form an anti-reflective coating layer dimishing light reflection of exposure light (I).

15. Method of producing an anti-reflective coating material (2) by

- providing a matrix material (3) and providing nano-crystalline particles (4) and
- mixing the matrix material (3) and the nano-crystalline particles (4) to form the anti-reflective coating material (2),

characterised in that
nano-crystalline particles (4) absorbing light via the quantum size effect are used.

16. Method according to claim 15,
characterised in that
the kind of the nano-crystalline particles (4) and/or the concentration of the nano-crystalline particles (4) in the

matrix material (3) is chosen such that an anti-reflective coating material (2) having an adjusted refractive index (ε1) is formed.

17. Method according to claim 15 or 16,
characterised in that
by choosing the kind and/or the concentration of the nano-crystalline particles (4) such a refractive index (ε1) is adjusted which depends on the refractive index (ε0) of a resist layer to be applied onto the anti-reflective coating material (2) and/or which depends on the refractive index (ε2) of a semiconductor substrate (1) to be patterned or of a layer (1) to be patterned on a semiconductor substrate.

18. Semiconductor product comprising a substrate (1) having a surface (11) with a layer of an anti-reflective coating material arranged on the surface (11),
characterised in that
the anti-reflective coating material is an anti-reflective coating material (2) according to one of claims 1 to 13.

19. Semiconductor product according to claim 18,
characterised in that
the semiconductor product comprises a resist layer (5) on top of the layer of the anti-reflective coating material (2).

FIG 1

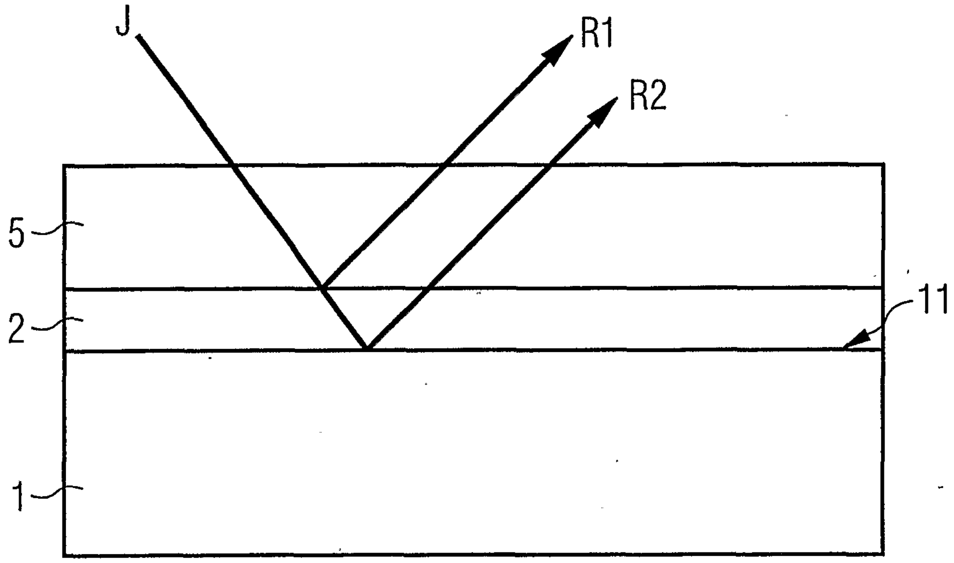


FIG 2

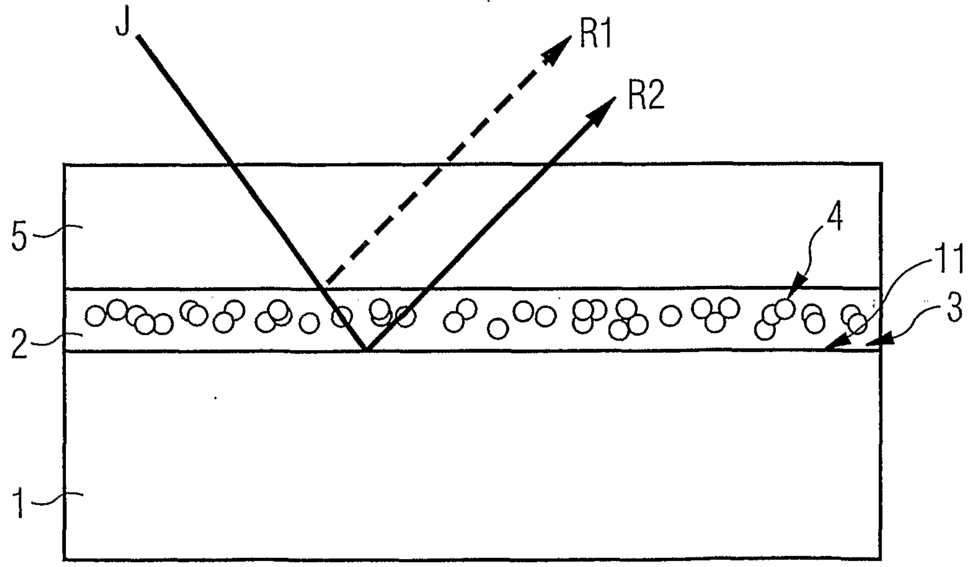


FIG 3