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(54) **METHOD FOR PREPARING SUBSTRATE WITH PERIODICAL STRUCTURE**

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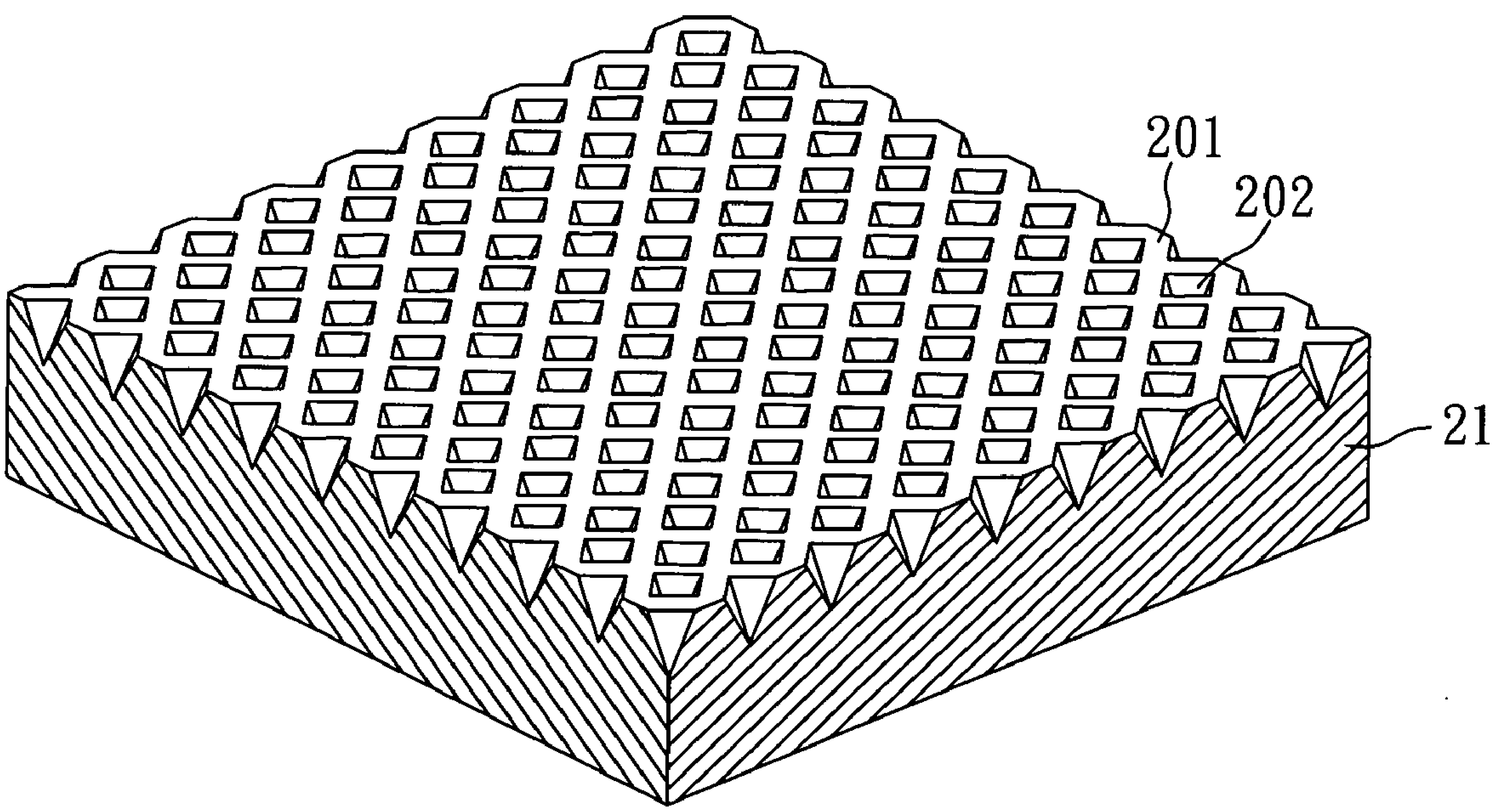
(57) **ABSTRACT**

A method for preparing a substrate with periodical structure, comprising the following steps: (A) providing a substrate and plural nano-sized balls, wherein the nano-sized balls are arranged on the surface of the substrate; (B) depositing a cladding layer on partial surface of the substrate and the gaps between the nano-sized balls; (C) removing the nano-sized balls; (D) etching the substrate by using the cladding layer as a mask; and (E) removing the mask to form a periodical structure on the surface of the substrate. In the present invention, the nano-sized balls are used as a template for forming the mask. Hence, compared with the lithography, when the method of the present invention is used to prepare a substrate with a periodical structure, the duration of the process and the manufacturing cost can be decreased.



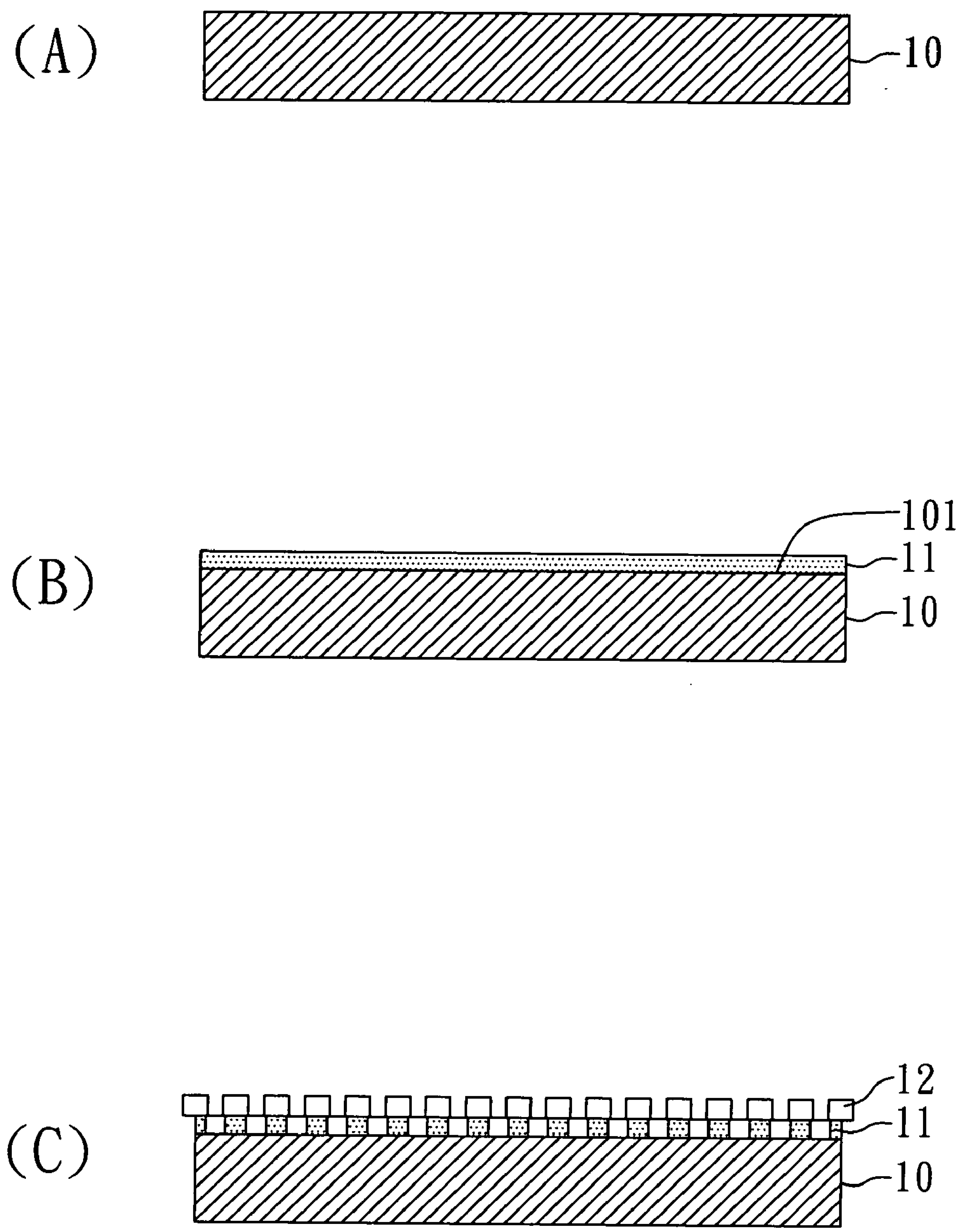
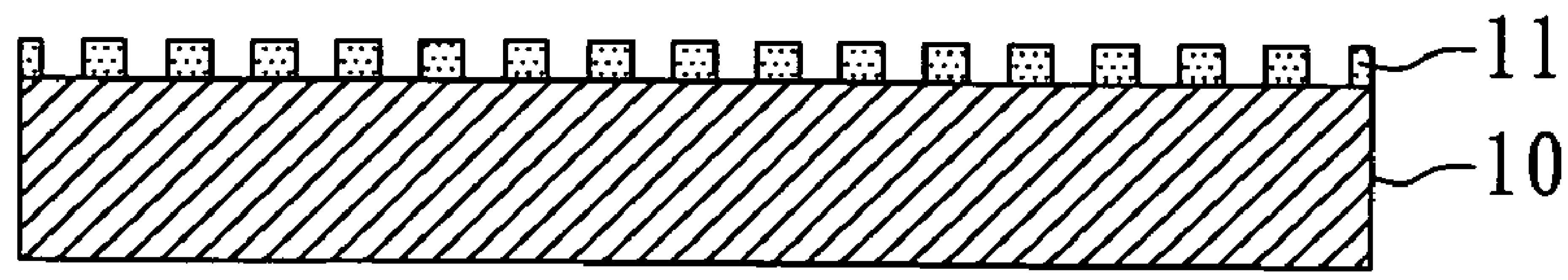
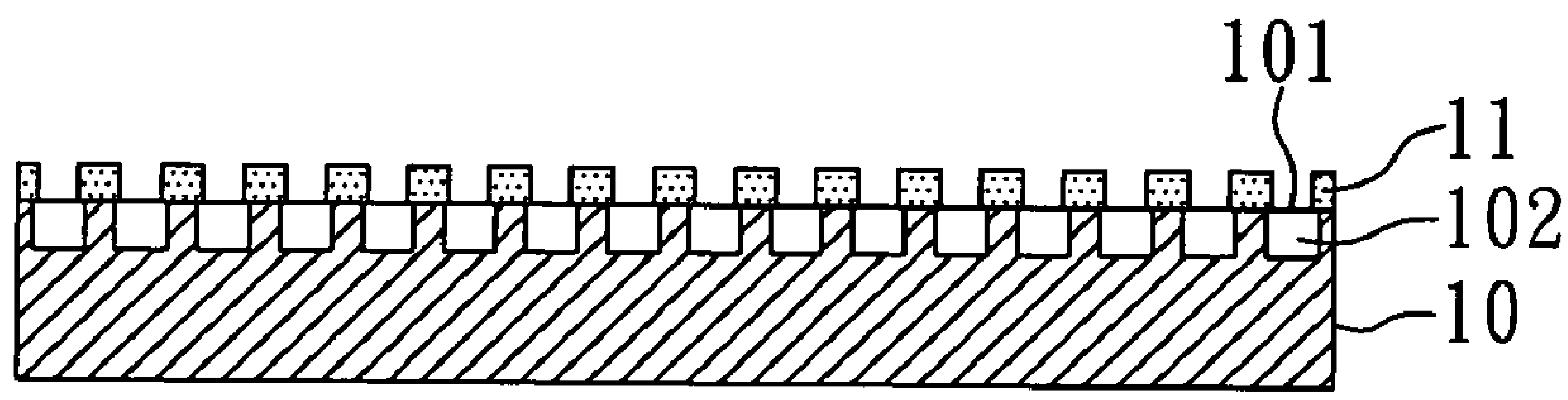


FIG. 1(PRIOR ART)

(D)



(E)



(F)

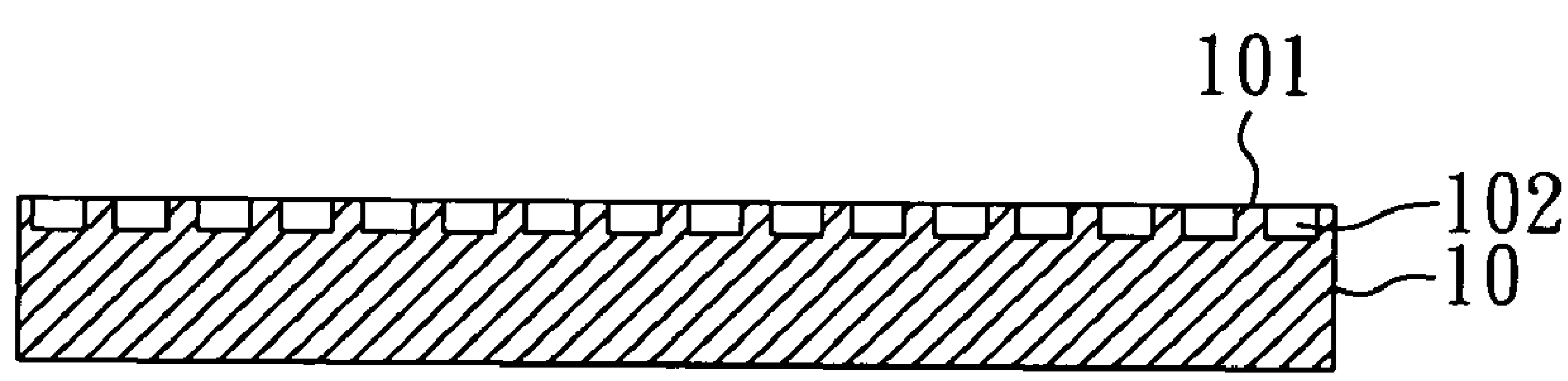


FIG. 1(PRIOR ART)

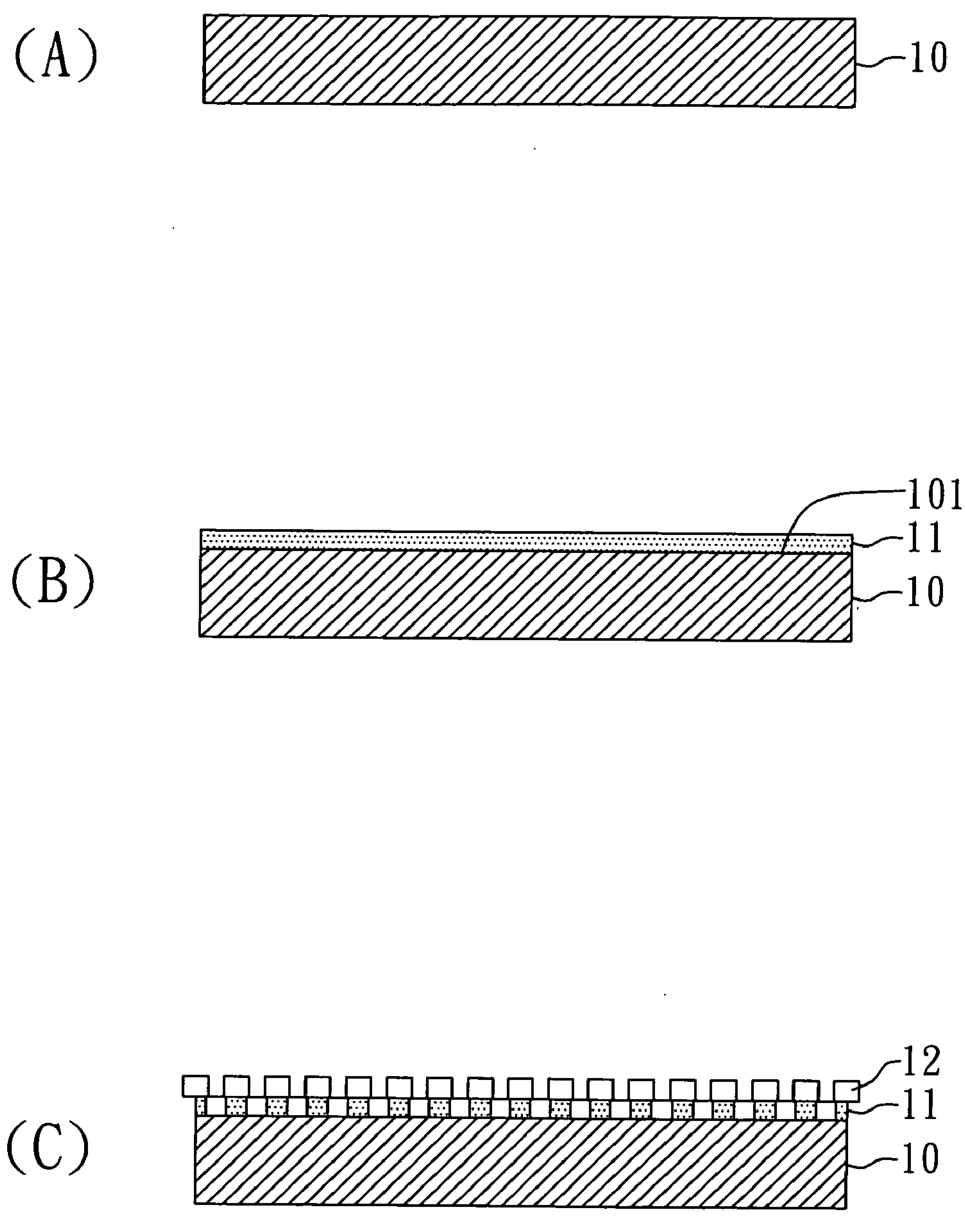


FIG. 2(PRIOR ART)

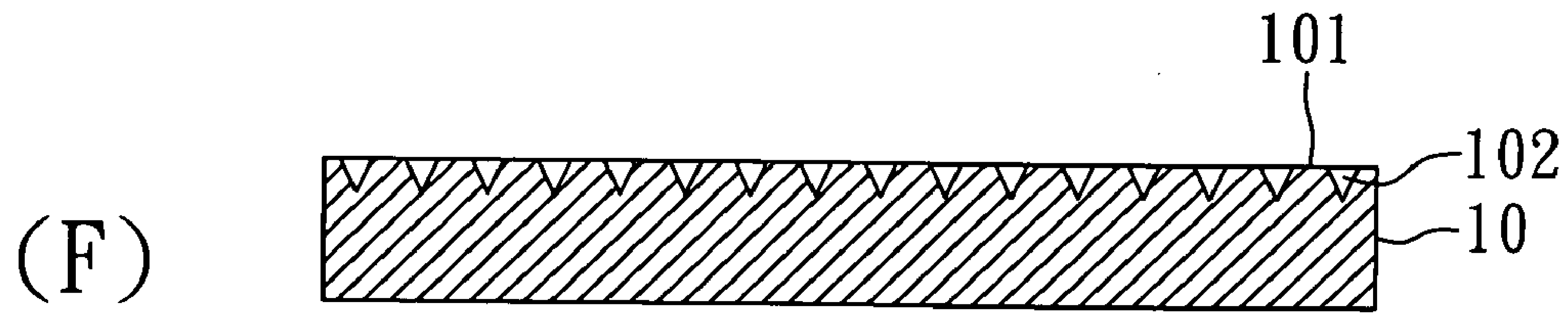
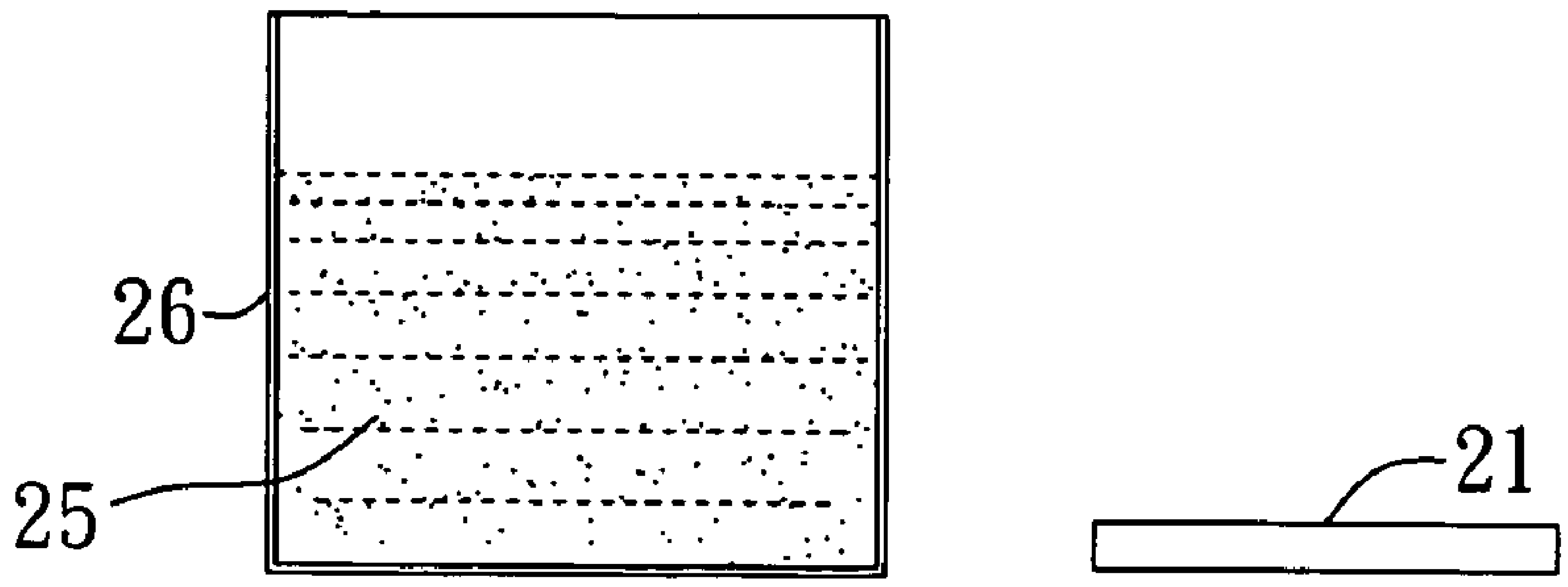
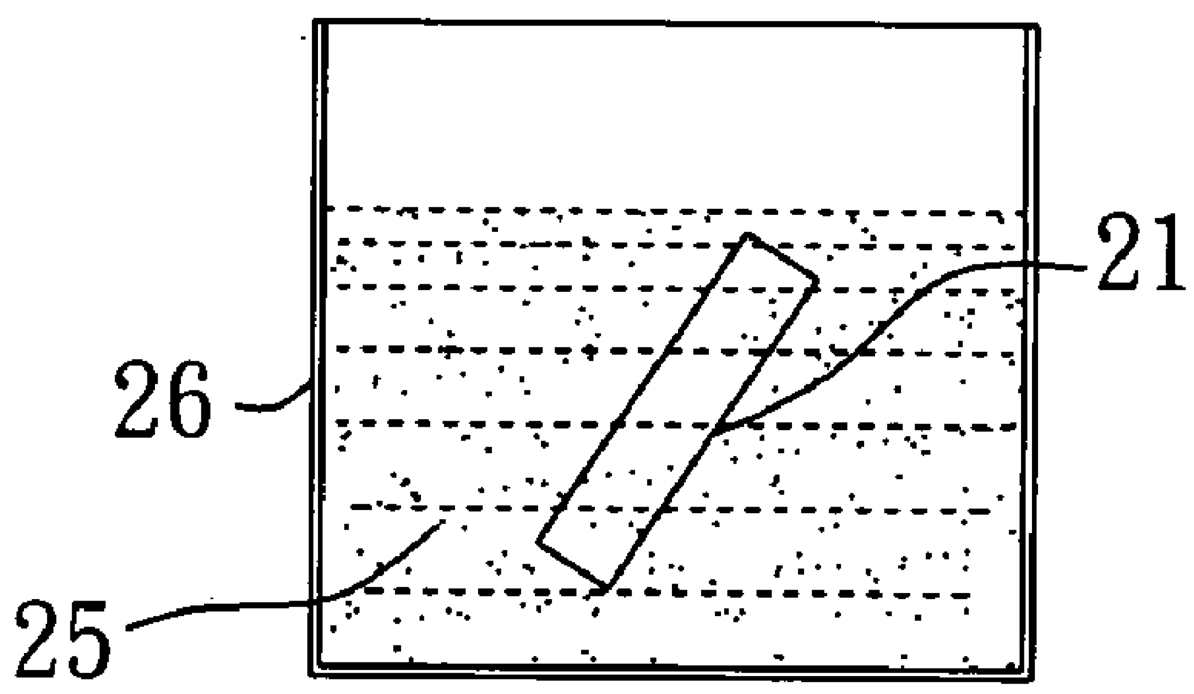


FIG. 2(PRIOR ART)

(A)



(B)



(C)

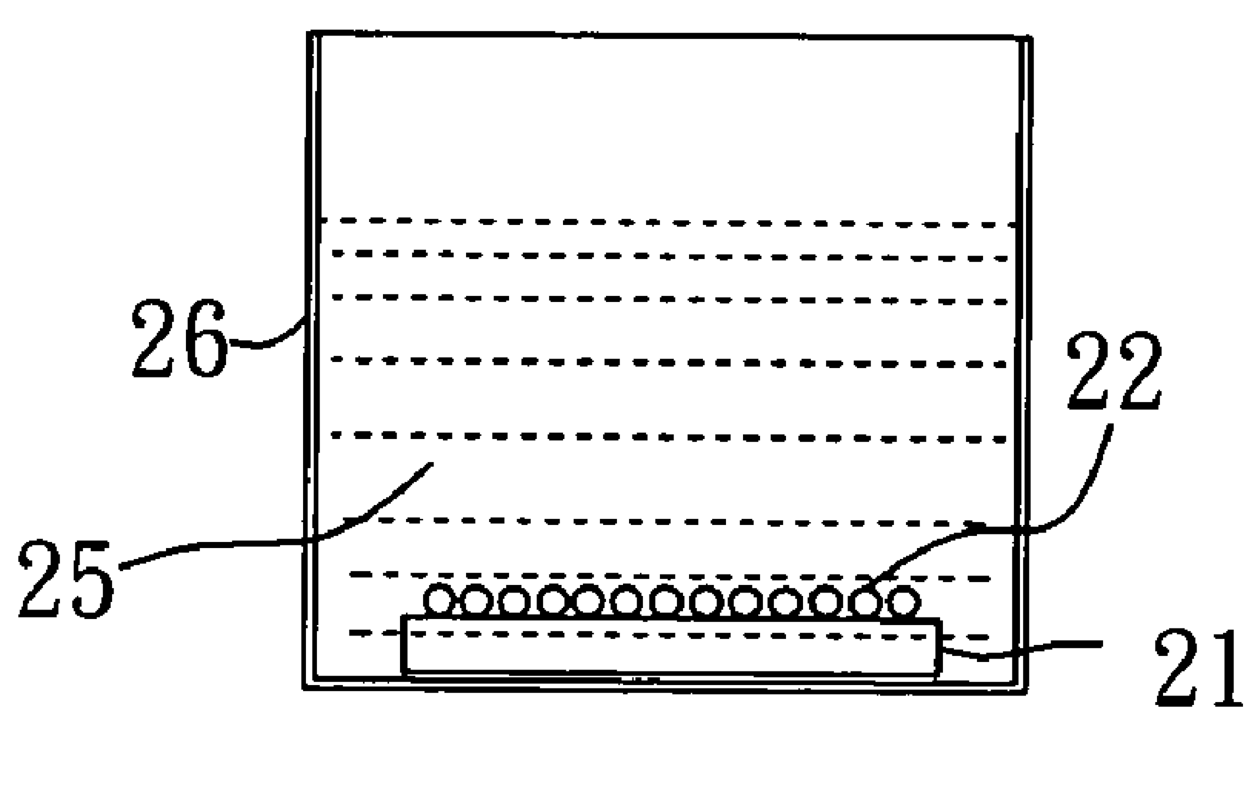


FIG. 3

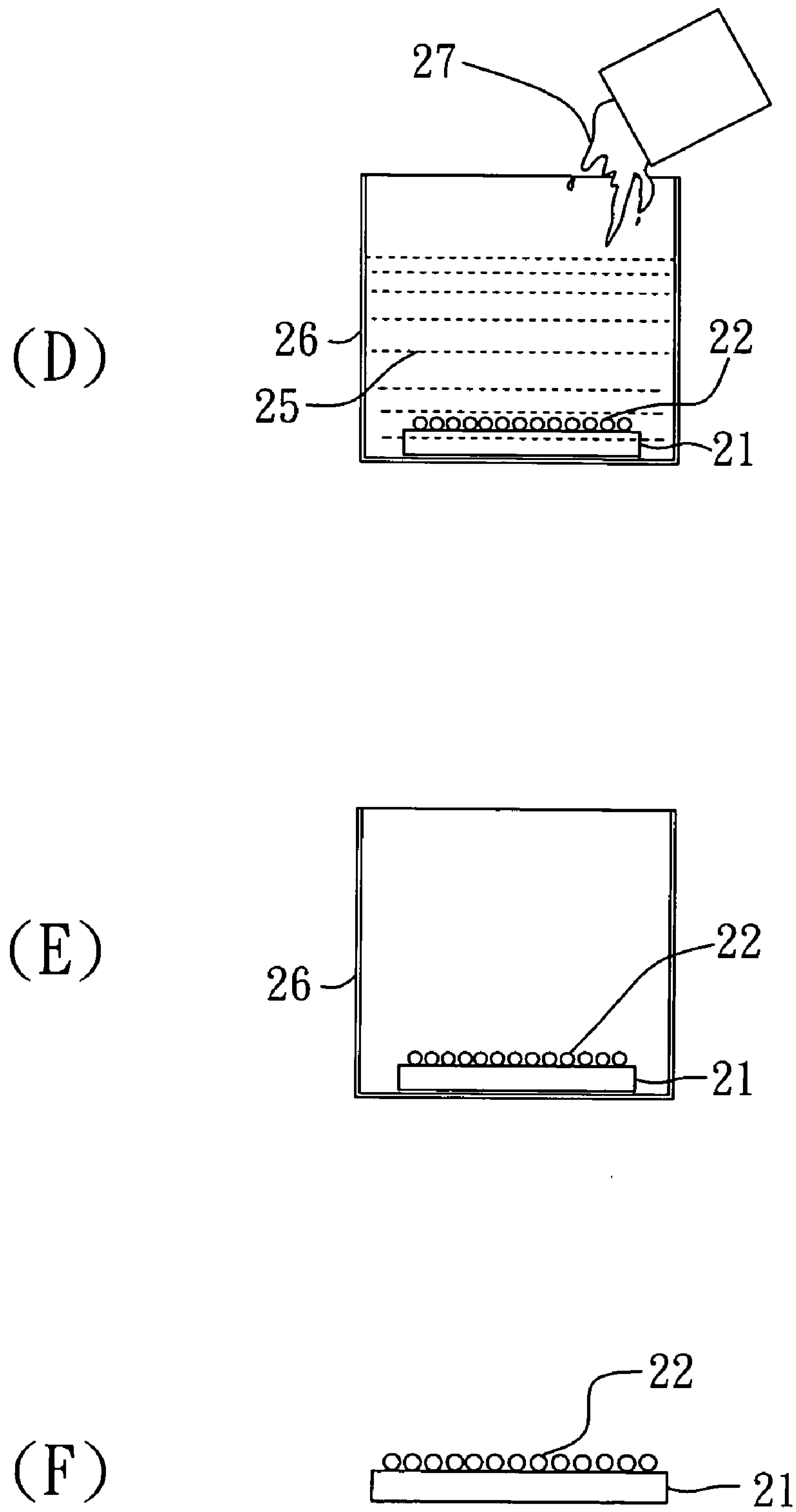


FIG. 3

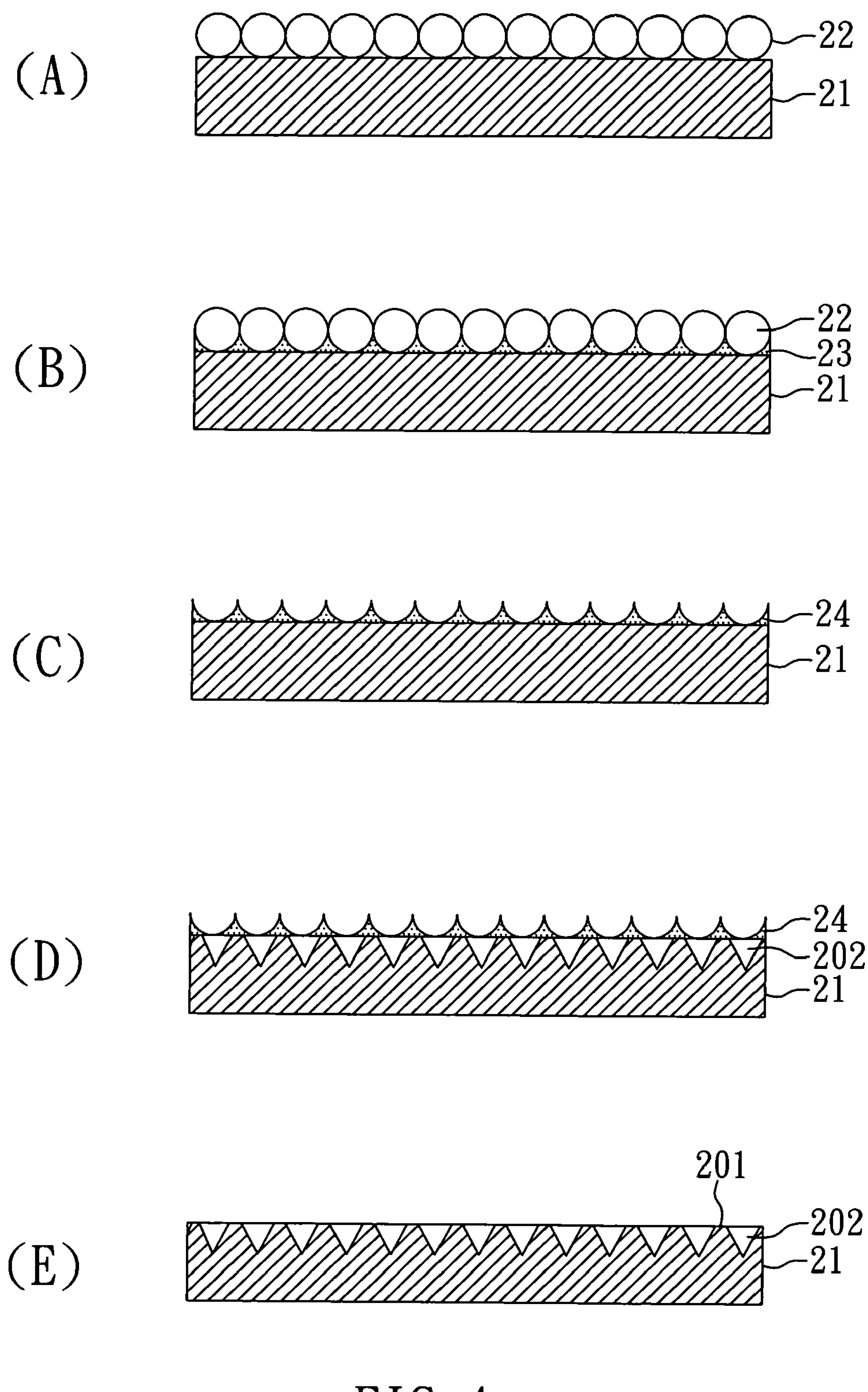


FIG. 4

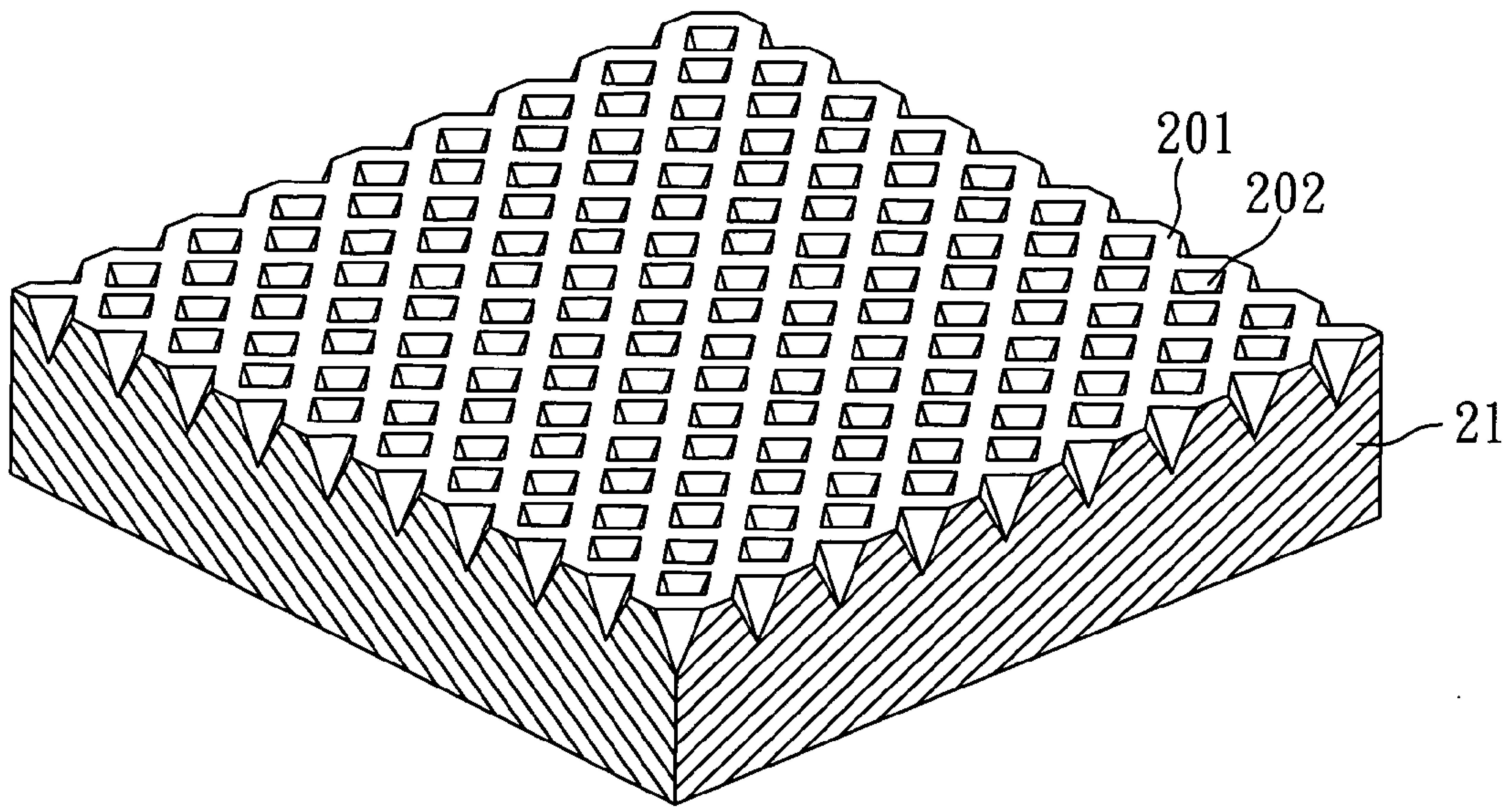


FIG. 5

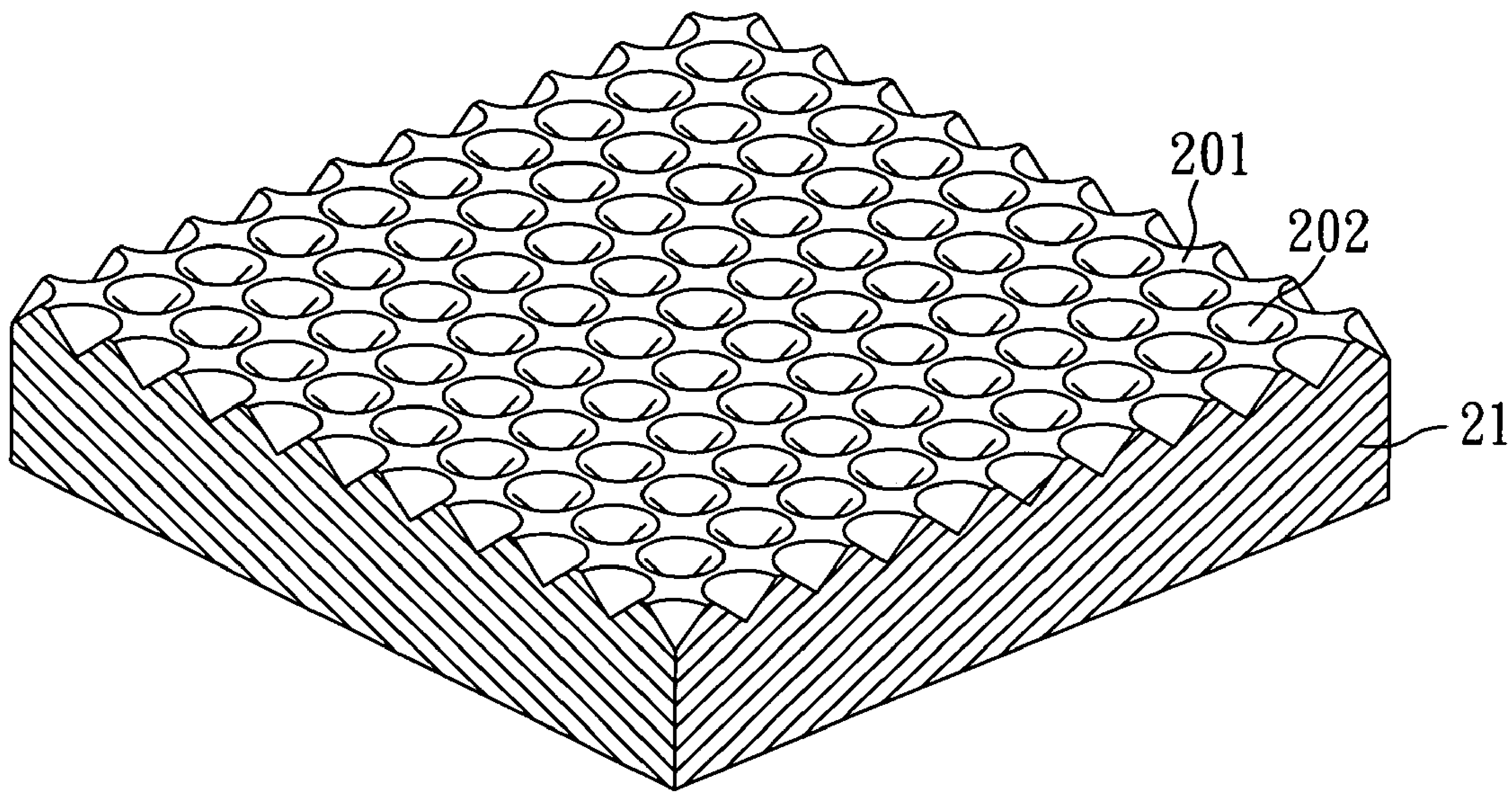


FIG. 6

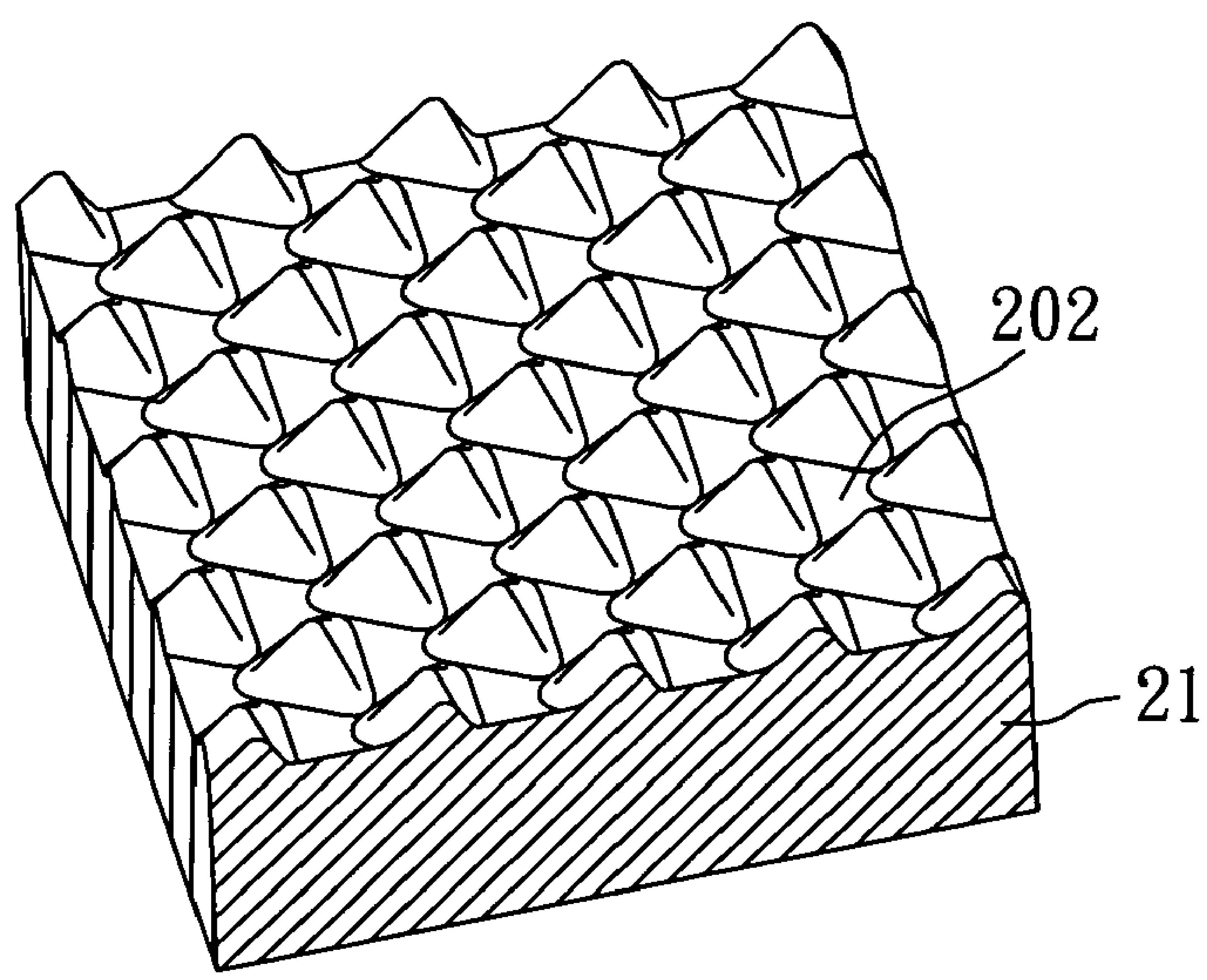


FIG. 7

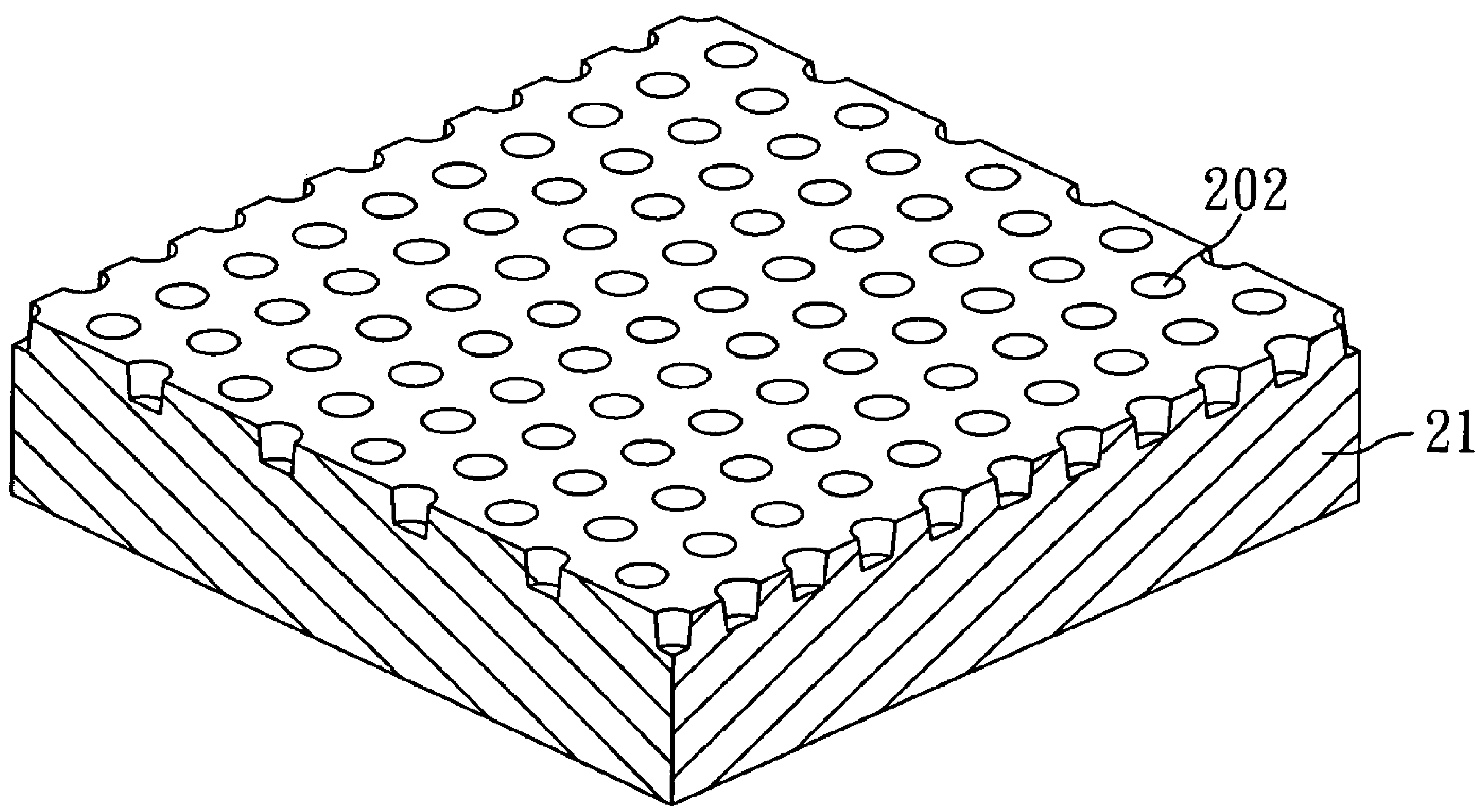


FIG. 8

METHOD FOR PREPARING SUBSTRATE WITH PERIODICAL STRUCTURE

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates to a method for preparing a substrate with a periodical structure and, more particularly, to a method, which can prepare a substrate with a periodical structure in a rapid and inexpensive way and protect the substrate from damage.

[0003] 2. Description of Related Art

[0004] A photonic crystal is a periodical structure, which can control and manipulate the flow of light having a certain frequency range, and also can prevent the propagation of light having other frequency ranges. The photonic crystals work at optical wavelengths, so the photonic crystals have to be formed of a periodic sub-micro sized or nano sized structure. Currently, the photonic crystals can be applied widely in the fields of optical communications and optical calculators, and also applied to photoelectric devices to improve the efficiency thereof.

[0005] The photonic crystals are generally manufactured by patterning a substrate through high-energy engraving process or nano-imprinting technology. The engraving process using laser, e-beams, or ion beams, or laser holographic interference lithography can be used for forming the photonic crystals. Alternatively, a hard template for preparing photonic crystals is formed by the aforementioned methods, and then the hard template is pressed on a soft matrix. However, high-energy engraving process has disadvantages of high manufacturing cost and low production capacity. Although nano-imprinting technology has lower manufacturing cost and higher production capacity than high-energy engraving process, it still cannot meet the requirements for low manufacturing cost and high production capacity.

[0006] Currently, a dry etching process or a wet etching process can be used for patterning a substrate to form a substrate with a periodical structure. The dry etching process for patterning the substrate is shown in FIGS. **1**A to **1**F. First, referring to FIG. **1**A, a substrate **10** is provided; and a photo-resist layer **11** is formed on the surface **101** of the substrate **10**, as shown in FIG. **1**B. Next, a photo-mask **12** is provided on the photo-resist layer **11**, followed by exposing to pattern the photo-resist layer **11**, as shown in FIG. **1**C. After developing the photo-resist layer **11** and removing the photo-mask **12**, a patterned photo-resist layer **11** is obtained, as shown in FIG. **1**D. A reactive ion etching (RIE) process is performed to etch the substrate **10** by using the patterned photo-resist layer **11** as an etching template, and then plural micro-cavities **102** are formed on the surface of the substrate **10**, as shown in FIG. **1**E. After removing the photo-resist layer **11** (i.e. the etching template), a patterned substrate **10** is obtained, as shown in FIG. **1**F. Herein, the plural micro-cavities formed on the surface **101** of the patterned substrate **10** are arranged in a periodical structure.

[0007] Although the method of dry etching can produce a substrate having a periodical structure with uniform and regular micro-cavities, there are still some disadvantages with the aforementioned process. First, the manufacturing cost of photolithography is high and the production rate is low. Further, if a nano-sized periodical structure is desired, a photo-mask with sub-micro size is required in the photolithography process. However, the photo-mask with sub-micro size is very expensive, and the manufacturing cost of the photo-mask is even more expensive when a periodical structure with a size of 500 nm or less is desired. In addition, the RIE machine is expensive, the RIE process is slow, and the substrate is damaged easily when the RIE process is used. Moreover, the etching surface formed through the dry etching process, i.e. the surface of the patterned substrate, is an unnatural lattice plane.

[0008] In order to solve the problem resulting from the dry etching process, a wet etching process is developed to form a substrate with a periodical structure. As shown in FIGS. **2**A to **2**F, a single crystalline silicon substrate in the <**100**> lattice direction is used for preparing a substrate with a periodical structure. The process for patterning the substrate by use of the wet etching process is similar to the aforementioned process, except an etching buffer is used for replacing the RIE process to etch the substrate. As shown in FIGS. **2**A to **2**D, after exposure and development processes, i.e. photolithography process, a patterned photo-resist layer **11** is formed (see FIG. **2**D). Then, a non-isotropic etching buffer is used to etch the substrate **10** by using the patterned photo-resist layer **11** as an etching template, and then plural micro-cavities **102** are formed on the surface of the substrate **10**, as shown in FIG. **2**E. After removing the photo-resist layer **11** (i.e. the etching template), a patterned substrate **10** is obtained, as shown in FIG. **2**F. Herein, the plural micro-cavities **102** formed on the surface **101** of the patterned substrate **10** are arranged in a periodical structure. It should be noted that the micro-cavities **102** formed by patterning the substrate **10** through the wet etching process are in inverted square pyramid-shapes. The sides of the inverted square pyramid are consistent with the lattice plane of a single crystalline silicon substrate <**111**>.

[0009] The wet etching process can protect the substrate from damage and the surface of the patterned substrate is a natural lattice plane, but the uniformity of the periodical structure is not good enough if the parameter of the wet etching process is not controlled properly. In addition, the photolithography is still performed in the aforementioned process, so the problems of high manufacturing cost and low production rate still exist.

[0010] Therefore, it is desirable to provide a method for patterning a substrate, which can protect the substrate from damage and form a periodical structure on the substrate in a rapid and inexpensive way.

SUMMARY OF THE INVENTION

[0011] The object of the present invention is to provide a method for preparing a substrate with a periodical structure formed thereon, in order to reduce the time and cost of production, and also prevent the substrate from being damaged.

[0012] To achieve the object, the method for preparing a substrate with a periodical structure of the present invention includes: (A) providing a substrate and plural nano-sized balls, wherein the nano-sized balls are arranged on a surface of the substrate; (B) depositing a cladding layer on partial surface of the substrate and the gaps between the nano-sized balls; (C) removing the nano-sized balls; (D) etching the substrate by using the cladding layer as an etching template; and (E) removing the etching template to form the periodical structure on the surface of the substrate.

[0013] According to the method of the present invention, the nano-sized balls arrange automatically and uniformly on the surface of the substrate. The well-arranged nano-sized balls can serve as a template for forming an etching template, to replace the process of photolithography. Because the expensive photo-mask with sub-micro size is not needed, the manufacturing cost of the substrate with the periodical structure can be reduced. Therefore, the method of the present invention can prepare the substrate with the periodical structure in a rapid and inexpensive way. In addition, the material used in the present invention can be obtained very easily, so the method of the present invention is suitable for forming the substrate with the periodical structure at a large scale.

[0014] According to the method of the present invention, the periodical structure on the surface of the substrate has plural micro-cavities. Preferably, the micro-cavities are arranged in an array. In addition, the shape of the micro-cavities is determined by the crystal lattice plane generated during the process of etching the substrate. The micro-cavities may be each in an inverted awl-shape, an inverted cone-shape, a cylinder-shape, an inverted truncated awl-shape, or an inverted truncated cone-shape. As the substrate and the etching buffer are different, the shape of the obtained micro-cavities is different. When an etching buffer containing NaOH is used to etch single crystalline silicon, the obtained micro-cavities are each in an inverted square pyramid-shape, wherein the base of the square pyramid is located on the surface of the substrate, and the apex of the square pyramid is hollowed from the surface of the substrate. When an etching buffer containing HF is used to etch a glass substrate, the obtained micro-cavities are each in an inverted truncated cone-shape.

[0015] According to the method of the present invention, after the step (E), the method further comprises a step (F): re-etching the surface of the substrate. The substrate with the periodical structure formed in the step (E) is a concaved substrate, wherein there is a plane between the adjacent micro-cavities. After re-etching the substrate in the step (F), the widths and the depths of the micro-cavities are increased. Therefore, the substrate with the periodical structure formed in the step (F) can be regarded as a convex substrate, wherein there is no plane between the adjacent micro-cavities.

[0016] According to the method of the present invention, the obtained periodical structure may be nano-sized of micro-sized periodical structure. Preferably, the periodical structure is nano-sized or submicro-sized periodical structure. More preferably, the periodical structure is nano-sized periodical structure.

[0017] According to the method of the present invention, step (A) of arranging the nano-sized balls on the surface of the substrate may comprise the following steps: (A1) providing the substrate, and a colloid solution in a container, wherein the colloid solution comprises the nano-sized balls and a surfactant; (A2) placing the substrate in the container, and the colloid solution covering the surface of the substrate; and (A3) adding a volatile solution into the container to obtain the substrate with the nano-sized balls formed thereon. The volatile solution can increase the vaporizing rate of the solution contained in the container. In addition, the nano-sized balls are arranged in nano-sized ball layers. Preferably, the nano-sized balls are arranged into one layer of nano-sized ball layer.

[0018] According to the method of the present invention, the process of dry etching or wet etching may be used for etching the substrate in the step (D). Preferably, the process of wet etching is used, wherein an etching buffer is used to etch the substrate. The type of the etching buffer is determined by the material of the substrate and the cladding layer. The etching buffer may be a general acidic or alkaline etching buffer. The acidic etching buffer may comprise an acidic solution, an alcohol, and water. Preferably, the acidic solution is HF, BOE which is a solution containing HF and NH_4F, HCl, HNO_3, H_2PO_4, H_2SO_4, CH_3COOH, or a combination thereof, or the acidic solution is Amine Callates containing ethanolamine, gallic acid, water, hydrogen peroxide, and a surfactant. In addition, the alkaline solution is a solution of NaOH, KOH, NH_4OH, CeOH, RbOH, $(CH_3)_4NOH$, $C_2H_4(NH_2)_2$, or N_2H_4, preferably. Furthermore, the alcohol is ethanol or isopropanol, preferably. Because the process of wet etching is used in the method of the present invention, it is possible to protect the substrate from damage.

[0019] According to the method of the present invention, the material of the nano-sized balls is not limited. Preferably, the material of the nano-sized balls is silicon oxides, ceramics, PMMA, titanium oxides, or PS. In addition, the diameters of the nano-sized balls may be 100 nm~2.5 μm. Preferably, the diameters of the nano-sized balls are 100 nm~1.2 μm, and the diameters of all the nano-sized balls are the same.

[0020] According to the method of the present invention, the method capable of forming the cladding layer in the step (B) is not limited. Preferably, chemical vapor deposition (CVD) or physical vapor deposition (PVD) is used to form the cladding layer on a partial surface of the substrate and the gaps between the nano-sized balls. In addition, the thickness of the cladding layer is determined by the desired size of the micro-cavities. Preferably, the thickness of the cladding layer is less than the diameters of the nano-sized balls. Furthermore, the material used in the cladding layer is not limited, and can be any material generally used for etching templates. Preferably, the material of the cladding layer is silicon oxides, silicon nitrides, silicon oxynitrides, Al_2O_3, ZnO, ITO, ZnO doped with Al, Cr, Ta, W, V, Ni, Sn, Fe, Cu, Mo, Ti, Al, Ag, Au, Pt, Pd, photoresist (PR), PMMA, or PS.

[0021] According to the method of the present invention, the material of the substrate is not limited, and can be determined by the application field of the substrate. The material of the substrate can be P-type single crystalline silicon, N-type single crystalline silicon, P-type polycrystalline silicon, N-type polycrystalline silicon, P-type amorphous silicon, N-type amorphous silicon, P-type GaAs, N-type GaAs, P-type InP, N-type InP, P-type GaInP, N-type GaAnP, P-type GaN, N-type GaN, P-type $CuInSe_2$, N-type $CuInSe_2$, ITO, silicon carbide, silicon nitride, quartz, ZnO, or ZnO doped with Al. Or, the substrate used in the method of the present invention can be a sapphire substrate, i.e. single crystalline Al_2O_3. Preferably, the substrate used in the method of the present invention is P-type silicon substrate, or a sapphire substrate.

[0022] In addition, a glass substrate, or a glass substrate with a transparent conducting oxide (TCO) layer formed thereon may also serve as the substrate used in the method of the present invention. When a glass substrate with a TCO layer formed thereon is used, the periodical structure can be formed on the TCO layer or on the surface of the glass substrate.

[0023] According to the method of the present invention, the nano-sized balls can serve as a template for forming an etching template. Hence, the photolithography process can be replaced by the process of forming the nano-sized ball layer. At the same time, the wet etching process is used in the present invention to etch the substrate, so it is possible to reduce the probability of damaging the substrate and obtain a substrate with a uniform periodical structure. Therefore, by using the method of the present invention, the substrate can be patterned to form the periodical structure thereon in a simple, inexpensive, and rapid way.

BRIEF DESCRIPTION OF THE DRAWINGS

[0024] FIGS. **1**A to **1**F are cross-sectional views illustrating a process for manufacturing a substrate with a periodical structure by use of a dry etching method in the art;

[0025] FIGS. **2**A to **2**F are cross-sectional views illustrating a process for manufacturing a substrate with a periodical structure by use of a non-isotropic wet etching method in the art;

[0026] FIGS. **3**A to **3**F are cross-sectional views illustrating a process that nano-sized balls are arranged on a surface of a substrate in a preferred embodiment of the present invention;

[0027] FIGS. **4**A to **4**E are cross-sectional views illustrating a process for manufacturing a substrate with a periodical structure in a preferred embodiment of the present invention;

[0028] FIG. **5** is a perspective view of a substrate with a periodical structure in a preferred embodiment of the present invention;

[0029] FIG. **6** is a perspective view of a substrate with a periodical structure in another preferred embodiment of the present invention;

[0030] FIG. **7** is a perspective view of a substrate with a periodical structure in a further preferred embodiment of the present invention; and

[0031] FIG. **8** is a perspective view of a substrate with a periodical structure in another further preferred embodiment of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0032] FIGS. **3**A to **3**F are cross-sectional views illustrating a process that nano-sized balls are arranged on a surface of a substrate in a preferred embodiment of the present invention. First, as shown in FIG. **3**A, a substrate **21** is provided, and a colloid solution **25** is provided in a container **26**, wherein the colloid solution **25** comprises plural nano-sized balls (not shown in the figure) and a surfactant (not shown in the figure). Next, the substrate **21** is placed in the container **26**, and the substrate **21** is immersed in the colloid solution **25** entirely, as shown in FIG. **3**B. After several minutes, the nano-sized balls **22** are arranged on the surface of the substrate **21** orderly to form a "nano-sized ball layer", as shown in FIG. **3**C. Then, a volatile solution **27** is added into the container **26** to evaporate the colloid solution **25**, as shown in FIG. **3**D. Finally, after the colloid solution **25** is evaporated completely, as shown in FIG. **3**E, the substrate **21** is taken out from the container **26**, and a substrate **21** with plural nano-sized balls **22** orderly arranged thereon is obtained, as shown in FIG. **3**F.

[0033] In the present embodiment, the material of the nano-sized balls **22** is poly-styrene (PS). However, the material of the nano-sized balls **22** can be ceramics, metal oxides such as TiO_x, poly(methyl methacrylate) (PMMA), or glass material such as SiO_x, according to different application demands. In addition, the diameters of the nano-sized balls **22** are 100 nm~2.5 μm, and the diameters of the majority of nano-sized balls **22** are the same. However, in different application demands, the sizes of the nano-sized balls **22** are not limited to the aforementioned range.

[0034] In the present embodiment, the material of the substrate is single crystalline silicon. However, the material of the substrate can be selected according to the application. For example, the material of the substrate may be P-type single crystalline silicon, N-type single crystalline silicon, P-type polycrystalline silicon, N-type polycrystalline silicon, P-type amorphous silicon, N-type amorphous silicon, P-type GaAs, N-type GaAs, P-type InP, N-type InP, P-type GaInP, N-type GaAnP, P-type GaN, N-type GaN, P-type $CuInSe_2$, N-type $CuInSe_2$, ITO, silicon carbide, silicon nitride, quartz, ZnO, or ZnO doped with Al; or the substrate may be a sapphire substrate made of single crystalline Al_2O_3, a glass substrate, or a glass substrate with a transparent conducting oxide (TCO) layer formed thereon.

[0035] FIGS. **4**A to **4**F are each cross-sectional views illustrating a process for manufacturing a substrate with a periodical structure in a preferred embodiment of the present invention.

[0036] First, as shown in FIG. **4**A, a substrate **21** and plural nano-sized balls **22** are provided. According to the aforementioned method, the nano-sized balls **22** are arranged in order on the surface of the substrate **21** to form a nano-sized ball layer. The nano-sized balls **22** may arrange on the surface of the substrate **21** in a form of multiple layers. In the present embodiment, the nano-sized balls **22** are arranged on the surface of the substrate **21** in a form of a single layer. The SEM image of the substrate **21** shows that the nano-sized balls are arranged on the surface of the substrate **21** in a form of a single layer.

[0037] Next, a cladding layer **23** is deposited on a partial surface of the substrate **21** and the gaps between the nano-sized balls **22** through CVD, as shown in FIG. **4**B. Herein, the thickness of the cladding layer **23** is less than the diameter of the nano-sized balls **22**. Further, the material of the cladding layer **23** is silicon nitride. However, the cladding layer **23** can be formed not only by CVD, but also by PVD. Moreover, the material of the cladding layer **23** can be any kind of material, which is ordinarily used to form an etching template. For example, the material of the cladding layer can be silicon oxides, silicon oxynitrides, Al_2O_3, ZnO, ITO, ZnO doped with Al, Cr, Ta, W, V, Ni, Sn, Fe, Cu, Mo, Ti, Al, Ag, Au, Pt, Pd, photoresist, PMMA, or PS.

[0038] Then, the nano-sized balls **22** are removed by using a THF solution, and the residual cladding layer **23** serves as an etching template **24**, as shown in FIG. **4**C. It should be noted that the nano-sized balls with different materials are removed from the substrate by different suitable solutions. For example, the nano-sized balls made of PMMA can be removed by toluene or formic acid, and the nano-sized balls made of SiO_x can be removed by using HF or a solution containing HF.

[0039] Then, as shown in FIG. **4**D, the cladding layer is used as an etching template **24** to pattern the substrate **21** through a method of wet etching. In the present embodiment, the etching buffer comprises NaOH, isopropanol, and water. However, the etching buffer used for wet etching is selected according to the material of the cladding layer and the substrate. For example, the etching buffer can be an alkaline etching buffer or an acidic etching buffer. The alkaline etching buffer may comprise: a solution of NaOH, KOH, NH_4OH, CeOH, RbOH, $(CH_3)_4NOH$, $C_2H_4(NH_2)_2$, or N_2H_4; an alcohol such as ethanol and isopropanol; and water. The acidic etching buffer may comprise: an acidic solution such as HF, BOE (a mixture of HF and NH_4F), HCl, HNO_3, H_2PO_4, H_2SO_4, CH_3COOH, and Amine Callates containing ethanolamine, gallic acid, water, hydrogen peroxide, and a surfactant; an alcohol such as ethanol and isopropanol; and water. In addition, as the components and the concentration of the etching buffer, and the temperature and the time of the etching process are changed, the patterns formed on the substrate are different. Furthermore, as the temperature of etching process is increased, the etching time is decreased.

[0040] After removing the etching template **24**, a periodical structure having plural micro-cavities **202** is formed on the surface **201** of the substrate **21**, as shown in FIG. **4**E. The micro-cavities **202** are arranged in an array. The material of the substrate **21** is single crystalline silicon, and the etching buffer used herein is a mixture containing NaOH, isopropanol and water. Hence, the micro-cavities **202** are each in an inverted square pyramid-shape, wherein the base of the square pyramid is located on the surface **201** of the substrate **21**, and the apex of the square pyramid is hollowed from the surface **201** of the substrate **21**. The SEM image of the substrate **21** shows that the micro-cavities are each in an inverted square pyramid-shape.

[0041] In order to understand the periodical structure formed on the substrate of the present embodiment, please refer to FIG. **5**, which is a perspective view of a substrate with a periodical structure in the preferred embodiment of the present invention. The substrate with the periodical structure prepared according to the aforementioned method comprises plural micro-cavities **202**, which are arranged in an array on the surface **201** of the sapphire substrate **21** and each formed in an inverted square pyramid-shape.

[0042] In the aforementioned preferred embodiment, the single crystalline silicon substrate is etched through the wet etching process, so the micro-cavities with inverted square pyramid-shapes are obtained. The shapes of the micro-cavities are determined by the lattice plane formed during the etching process. Hence, when the substrate and the etching buffer are different, the shapes of the micro-cavities are changed.

[0043] In another embodiment of the present invention, the same method as illustrated in the aforementioned embodiment is used to prepare a substrate with a periodical structure, except that the single crystalline substrate is replaced with a sapphire substrate. In the present embodiment, the etching buffer is a mixture of H_2SO_4 and H_2PO_4. After the etching process, micro-cavities with inverted awl-shape are obtained, as shown in FIG. **6**. Herein, there is a plane **201** between the adjacent two micro-cavities **202**, and the whole plane **201** is in a same elevation. Hence, the sapphire substrate prepared in the present embodiment is a concaved sapphire substrate with a periodical structure formed thereon. After SEM detection, the length from the side of the base to the projection point of the apex on the base is about 310 nm, and the length of the side of the base is about 410 nm. Hence, the concaved sapphire substrate prepared in the present invention has a nano-sized periodical structure formed thereon.

[0044] In addition, in a further preferred embodiment of the present invention, the concaved sapphire substrate prepared above is re-etched to enhance the roughness of the surface of the sapphire substrate. After re-etching the sapphire substrate, the size of the micro-cavities **202** is extended, and the depth of the micro-cavities **202** is increased. Further, the plane between the adjacent micro-cavities **202** is eliminated through the re-etching process. Hence, a convex sapphire substrate with a periodical structure is obtained, as shown in FIG. **7**.

[0045] Besides, in another further preferred embodiment of the present invention, the same method as illustrated in the aforementioned embodiment is used to prepare a substrate with a periodical structure, except that the single crystalline substrate is replaced with a glass substrate. Furthermore, a solution containing HF is used as an etching buffer. Because the etching buffer containing HF etches the substrate isotropically, the obtained micro-cavities **202** are in inverted truncated cone-shapes, as shown in FIG. **8**.

[0046] When the substrate with the periodical structure is prepared through photolithography and the wet etching process, it is difficult to obtain a nano-sized periodical structure. Although the dry etching process can be used to prepare the nano-sized periodical structure, the cost is high and the process is very complex. In addition, when the sapphire substrate with the periodical structure is prepared by a conventional process, a nano-sized periodical structure cannot be obtained. On the contrary, nano-sized balls, which can arrange orderly on the surface of the substrate, are used in the present invention to prepare a substrate with a periodical structure. Furthermore, the size of the micro-cavities of the substrate can be determined by the diameters of the nano-sized balls, in order to produce the substrate for different application. Also, when the size of the nano-sized balls is small enough, a nano-sized periodical structure can be prepared easily. In addition, compared to the engraving process using e-beams to form the periodical structure, the method of the present invention can reduce the manufacturing cost greatly. Also, when the photolithography, i.e. exposing and development is used to prepare the etching template, a photo-mask with sub-micro size is required. However, according to the method of the present invention, the nano-sized balls, which are simpler and easier than the photo-mask, are used to prepare the etching template. Hence, the manufacturing cost can be reduced and the production rate can be increased greatly. Furthermore, the RIE or ICP machine used in the dry etching process is very expensive and dangerous, but the tank for the wet etching process is cheap and safe. Additionally, when the dry etching process is used to form the periodical structure, the substrate may be damaged easily. However, according to the method of the present invention, the wet etching process is used to form the periodical structure, so it is possible to protect the substrate from damage. Therefore, the method of the present invention can prepare a substrate with a periodical structure in a simple, rapid, and inexpensive way, so the manufacturing cost can be reduced and the production rate can be increased.

[0047] Although the present invention has been explained in relation to its preferred embodiment, it is to be understood that many other possible modifications and variations can be made without departing from the scope of the invention as hereinafter claimed.

What is claimed is:

1. A method for preparing a substrate with a periodical structure, comprising:

(A) providing a substrate and plural nano-sized balls, wherein the nano-sized balls are arranged on a surface of the substrate;

(B) depositing a cladding layer on a partial surface of the substrate and the gaps between the nano-sized balls;

(C) removing the nano-sized balls;

(D) etching the substrate by using the cladding layer as an etching template; and

(E) removing the etching template to form the periodical structure on the surface of the substrate.

2. The method as claimed in claim **1**, further comprising a step (F) after the step (E): re-etching the surface of the substrate.

3. The method as claimed in claim **1**, wherein the periodical structure is a nano-sized periodical structure.

4. The method as claimed in claim **1**, wherein the step (A) of arranging the nano-sized balls on the surface of the substrate comprises the following steps:

(A1) providing the substrate, and a colloid solution in a container, wherein the colloid solution comprises the nano-sized balls and a surfactant;

(A2) placing the substrate in the container, and the colloid solution covering the surface of the substrate; and

(A3) adding a volatile solution into the container to obtain the substrate with the nano-sized balls formed thereon.

5. The method as claimed in claim **1**, wherein the cladding layer is formed on partial surface of the substrate and the gaps between the nano-sized balls through CVD or PVD.

6. The method as claimed in claim **1**, wherein the substrate is etched by an etching buffer in the step (D).

7. The method as claimed in claim **6**, wherein the etching buffer comprises an alkaline solution, an alcohol, and water.

8. The method as claimed in claim **6**, wherein the etching buffer comprises an acidic solution, an alcohol, and water.

9. The method as claimed in claim **7**, wherein the alkaline solution is a solution of NaOH, KOH, NH_4OH, CeOH, RbOH, $(CH_3)_4NOH$, $C_2H_4(NH_2)_2$, or N_2H_4.

10. The method as claimed in claim **7**, wherein the alcohol is ethanol or isopropanol.

11. The method as claimed in claim **8**, wherein the acidic solution is HF, BOE containing HF and NH_4F, HCl, HNO_3, H_2PO_4, H_2SO_4, CH_3COOH, or a combination thereof, or the acidic solution is Amine Callates containing ethanolamine, gallic acid, water, hydrogen peroxide, and a surfactant.

12. The method as claimed in claim **8**, wherein the alcohol is ethanol or isopropanol.

13. The method as claimed in claim **1**, wherein the periodical structure on the surface of the substrate has plural micro-cavities.

14. The method as claimed in claim **13**, wherein the micro-cavities are arranged in an array.

15. The method as claimed in claim **13**, wherein the micro-cavities are each in an inverted awl-shape, an inverted cone-shape, a cylinder-shape, an inverted truncated awl-shape, or an inverted truncated cone-shape.

16. The method as claimed in claim **1**, wherein the material of the substrate is P-type single crystalline silicon, N-type single crystalline silicon, P-type polycrystalline silicon, N-type polycrystalline silicon, P-type amorphous silicon, N-type amorphous silicon, P-type GaAs, N-type GaAs, P-type InP, N-type InP, P-type GaInP, N-type GaAnP, P-type GaN, N-type GaN, P-type $CuInSe_2$, N-type $CuInSe_2$, ITO, silicon carbide, silicon nitride, quartz, ZnO, or ZnO doped with Al.

17. The method as claimed in claim **1**, wherein the substrate is a sapphire substrate.

18. The method as claimed in claim **1**, wherein the substrate is a glass substrate, or a glass substrate with a transparent conducting oxide (TCO) layer formed thereon.

19. The method as claimed in claim **1**, wherein the material of the cladding layer is silicon oxides, silicon nitrides, silicon oxynitrides, Al_2O_3, ZnO, ITO, ZnO doped with Al, Cr, Ta, W, V, Ni, Sn, Fe, Cu, Mo, Ti, Al, Ag, Au, Pt, Pd, photoresist, PMMA, or PS.

20. The method as claimed in claim **1**, wherein the material of the nano-sized balls is silicon oxides, ceramics, PMMA, titanium oxides, or PS.

21. The method as claimed in claim **1**, wherein the thickness of the cladding layer is less than the diameters of the nano-sized balls.

22. The method as claimed in claim **1**, wherein the diameters of the nano-sized balls are 100 nm~2.5 μm.

23. The method as claimed in claim **1**, wherein the diameters of the nano-sized balls are the same.

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