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(19) **United States**(12) **Patent Application Publication**  
Nitta et al.(10) **Pub. No.: US 2004/0262163 A1**(43) **Pub. Date: Dec. 30, 2004**(54) **MOLTEN SALT BATH FOR  
ELECTROFORMING AND METHOD OF  
MANUFACTURING METAL PRODUCT  
USING THE SAME****Publication Classification**(51) **Int. Cl.<sup>7</sup> ..... C25D 1/00**(52) **U.S. Cl. .... 205/67**(75) **Inventors: Koji Nitta, Osaka (JP); Shinji  
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A molten salt bath for electroforming containing lithium bromide, cesium bromide and a halide of an alkali metal and/or a halide of an alkaline-earth metal is provided. In addition, a method of manufacturing a metal product including the steps of: forming a resist pattern on a conductive substrate and exposing a portion of the conductive substrate; immersing the conductive substrate having the resist pattern formed into the molten salt bath for electroforming, the molten salt bath for electroforming containing a metal to be precipitated and/or a compound of a metal to be precipitated; and precipitating the metal at a portion where the conductive substrate is exposed, is provided. Further, a molten salt bath for electroforming obtained by mixing lithium bromide, cesium bromide, and a halide of an alkali metal and/or a halide of an alkaline-earth metal is provided.

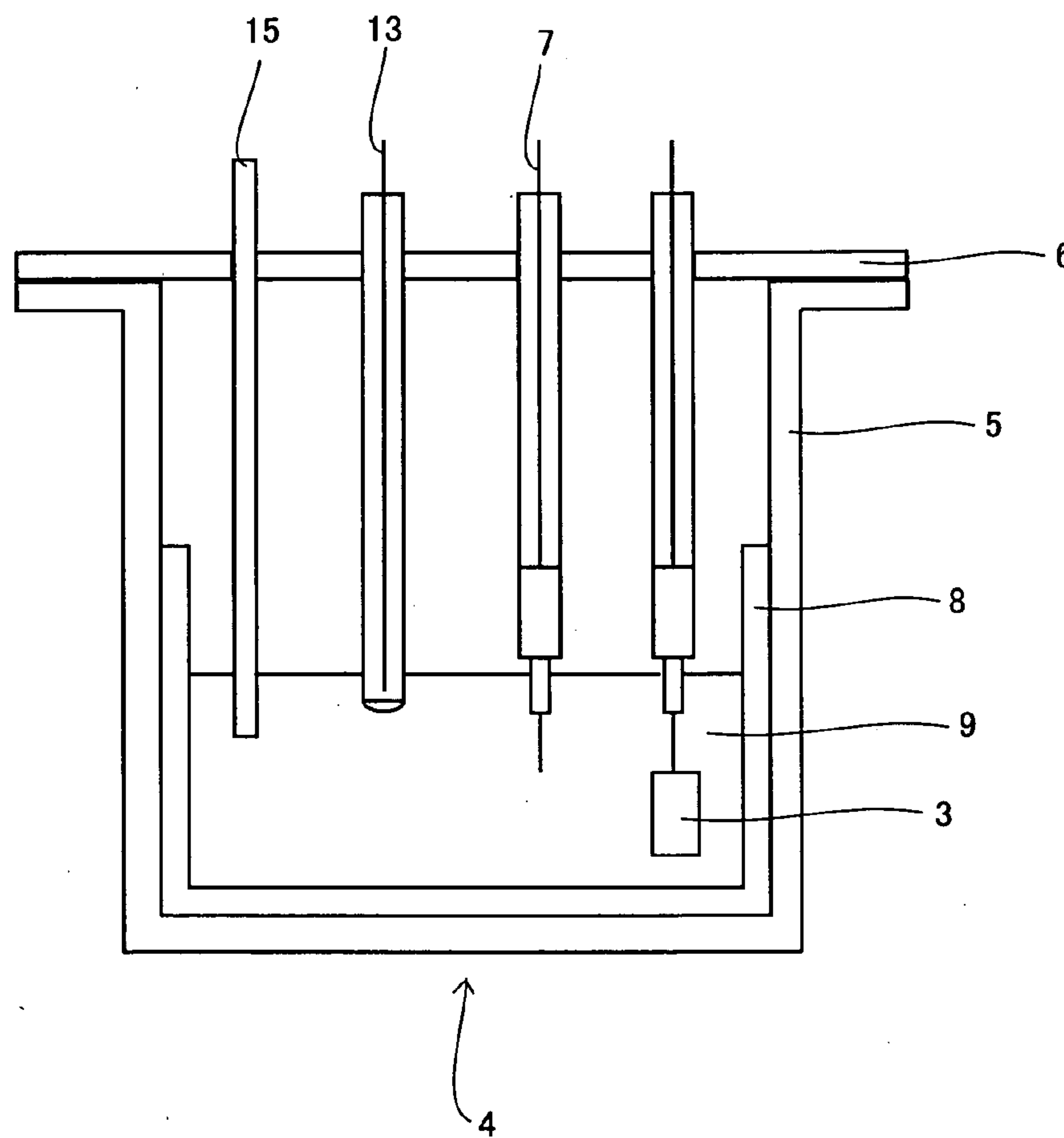


FIG.1A

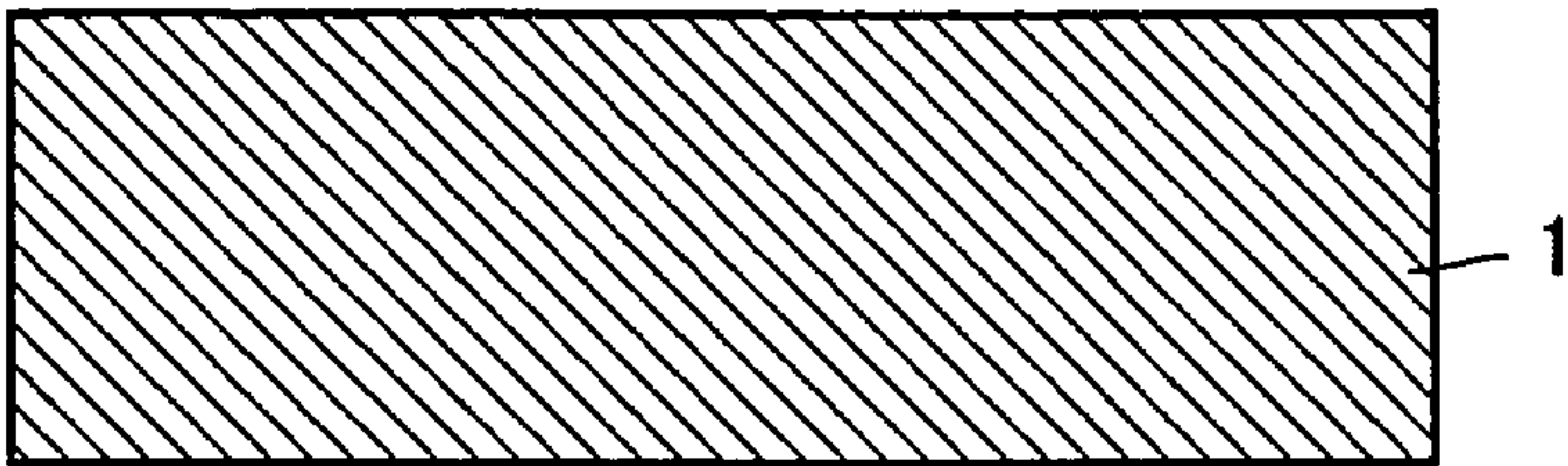


FIG.1B

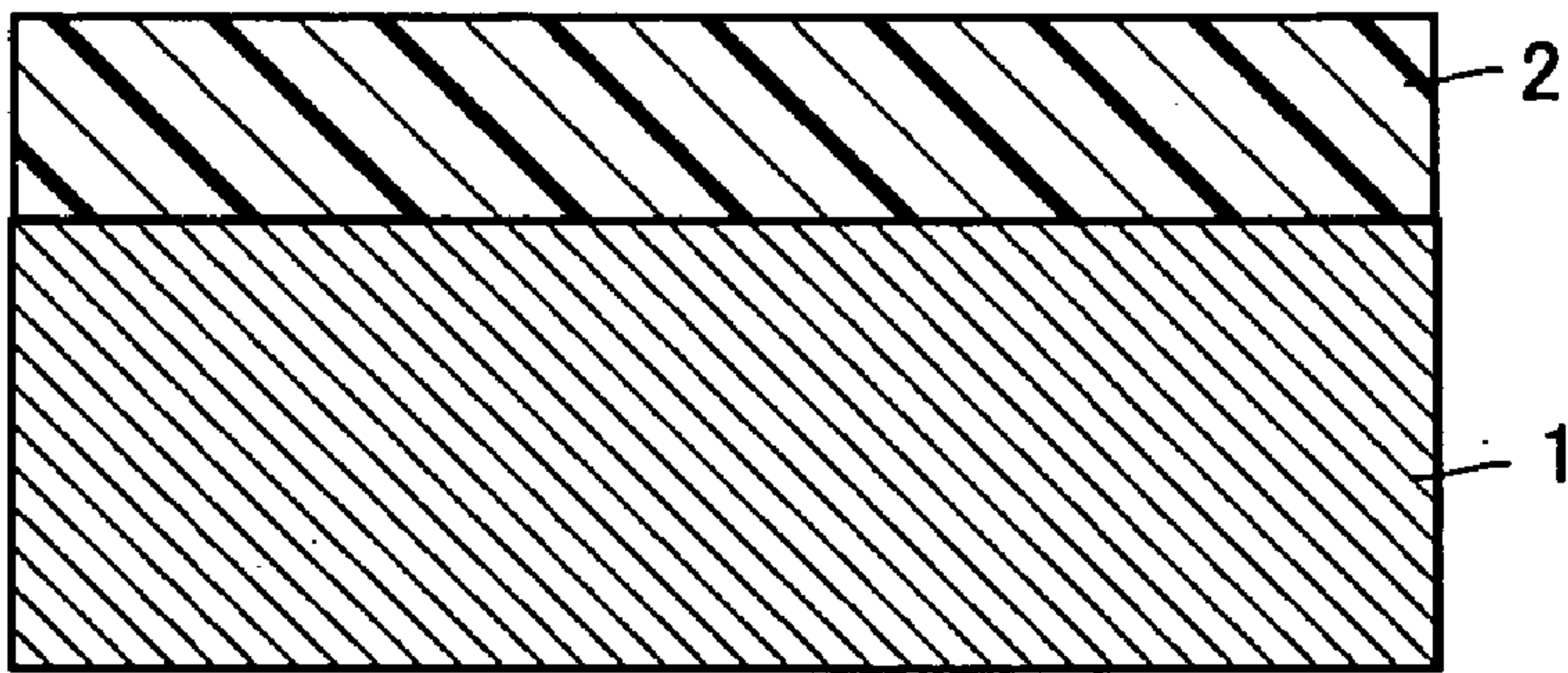


FIG.1C

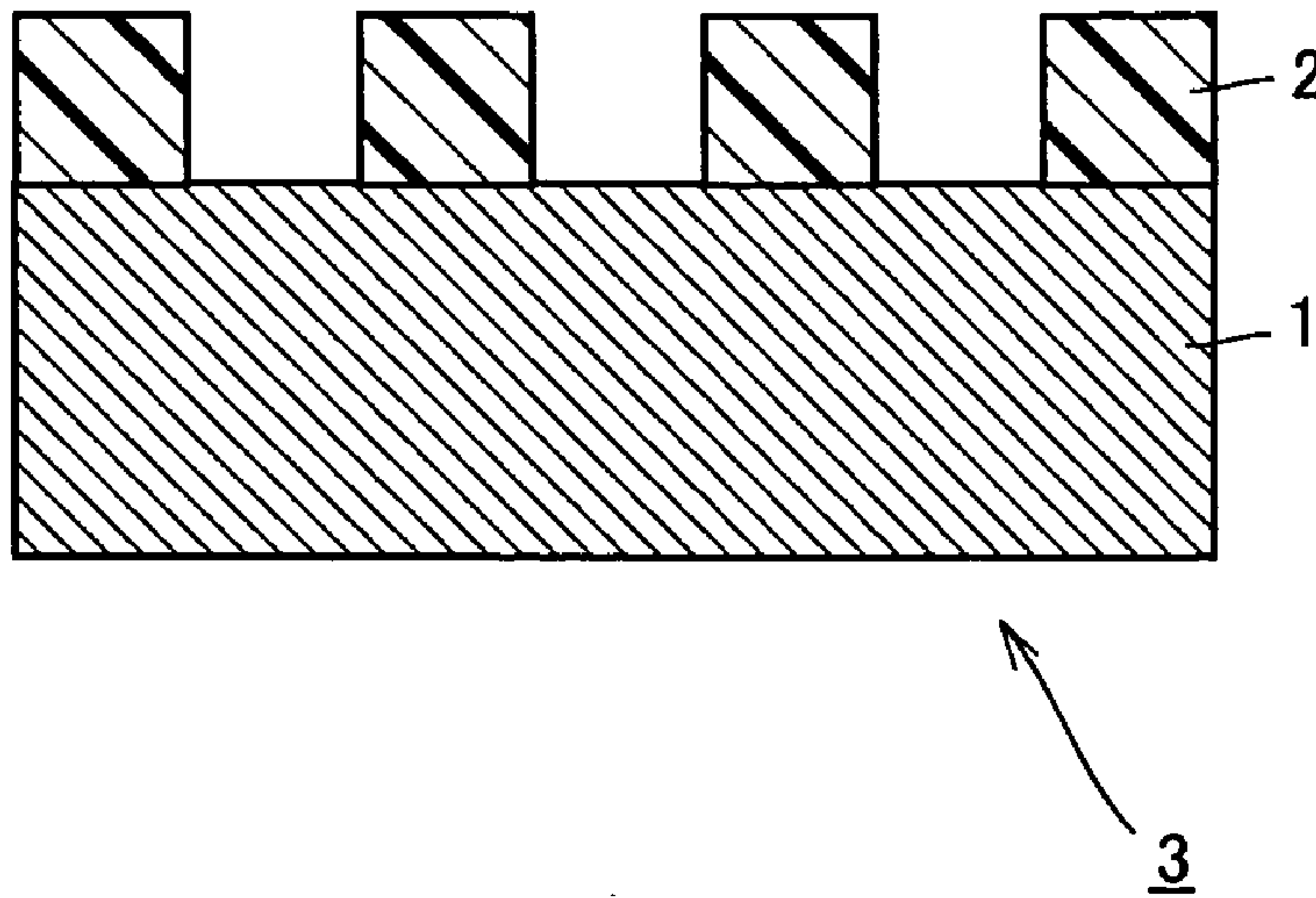


FIG.2

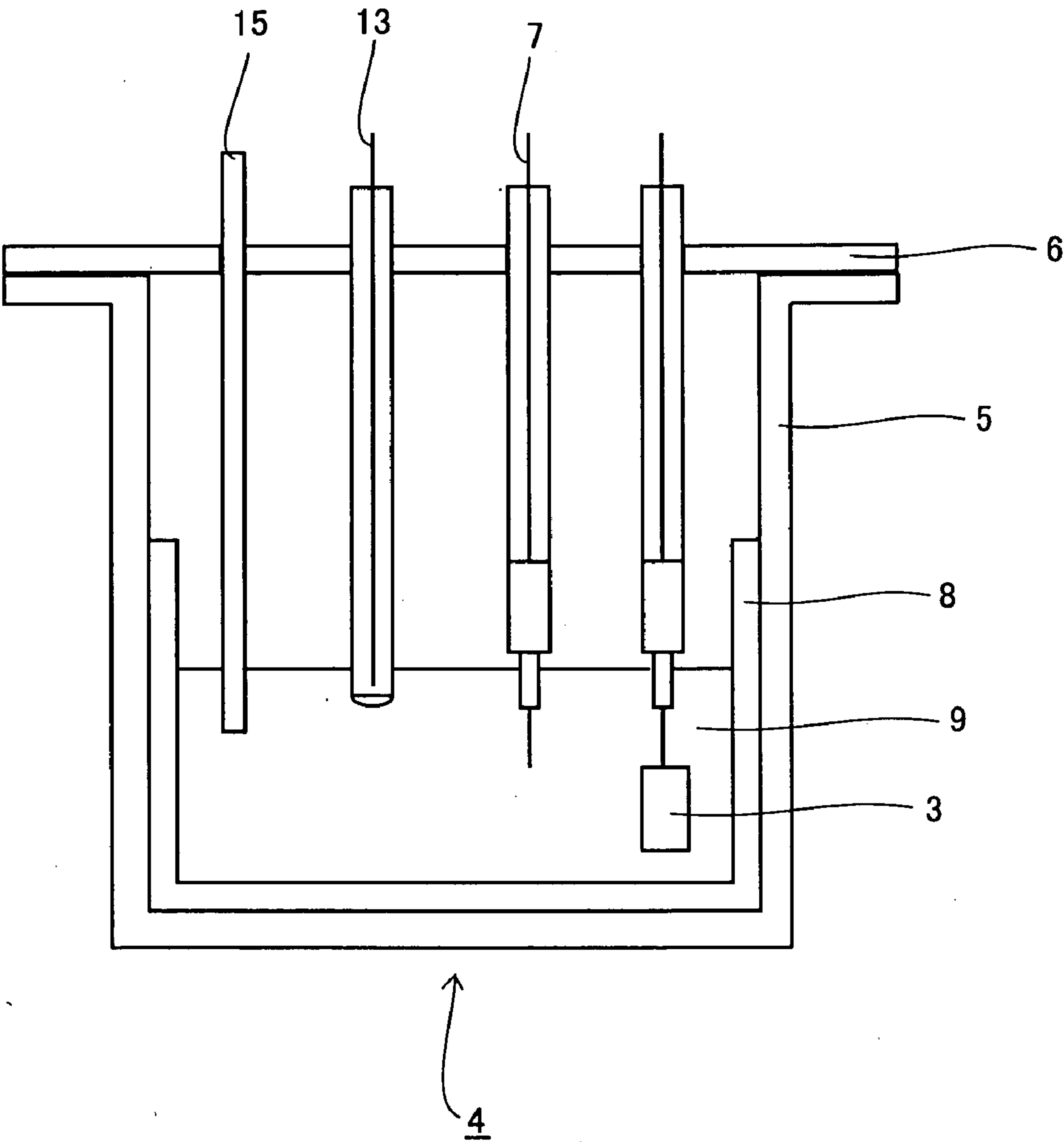


FIG.3

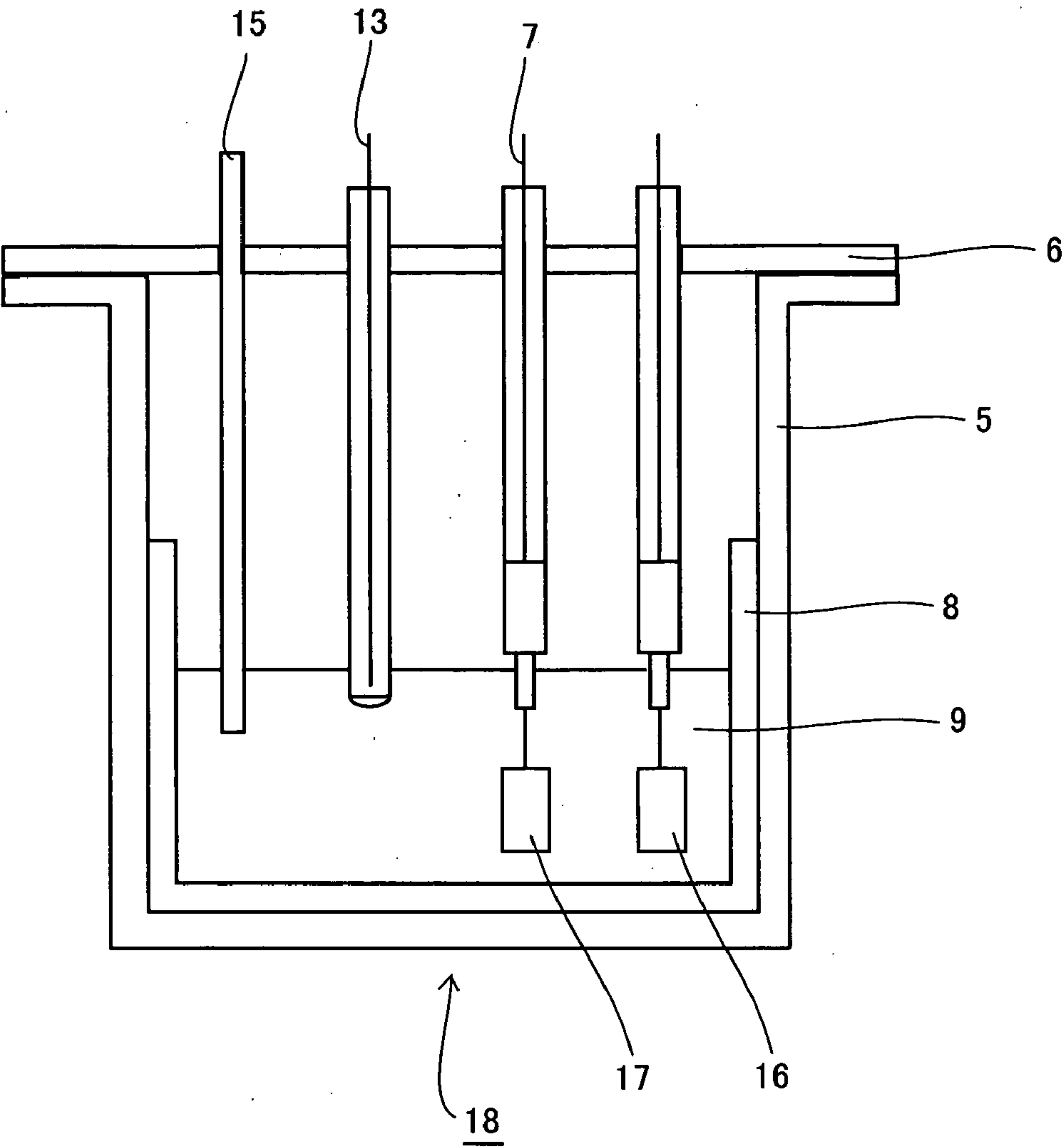


FIG.4A PRIOR ART

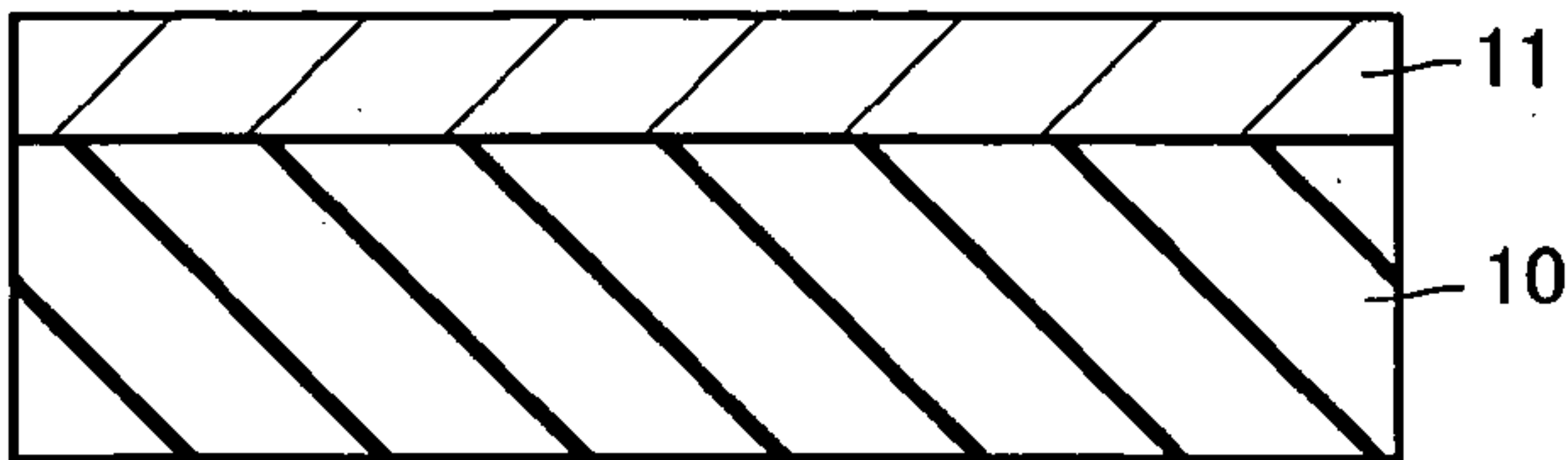


FIG.4B PRIOR ART

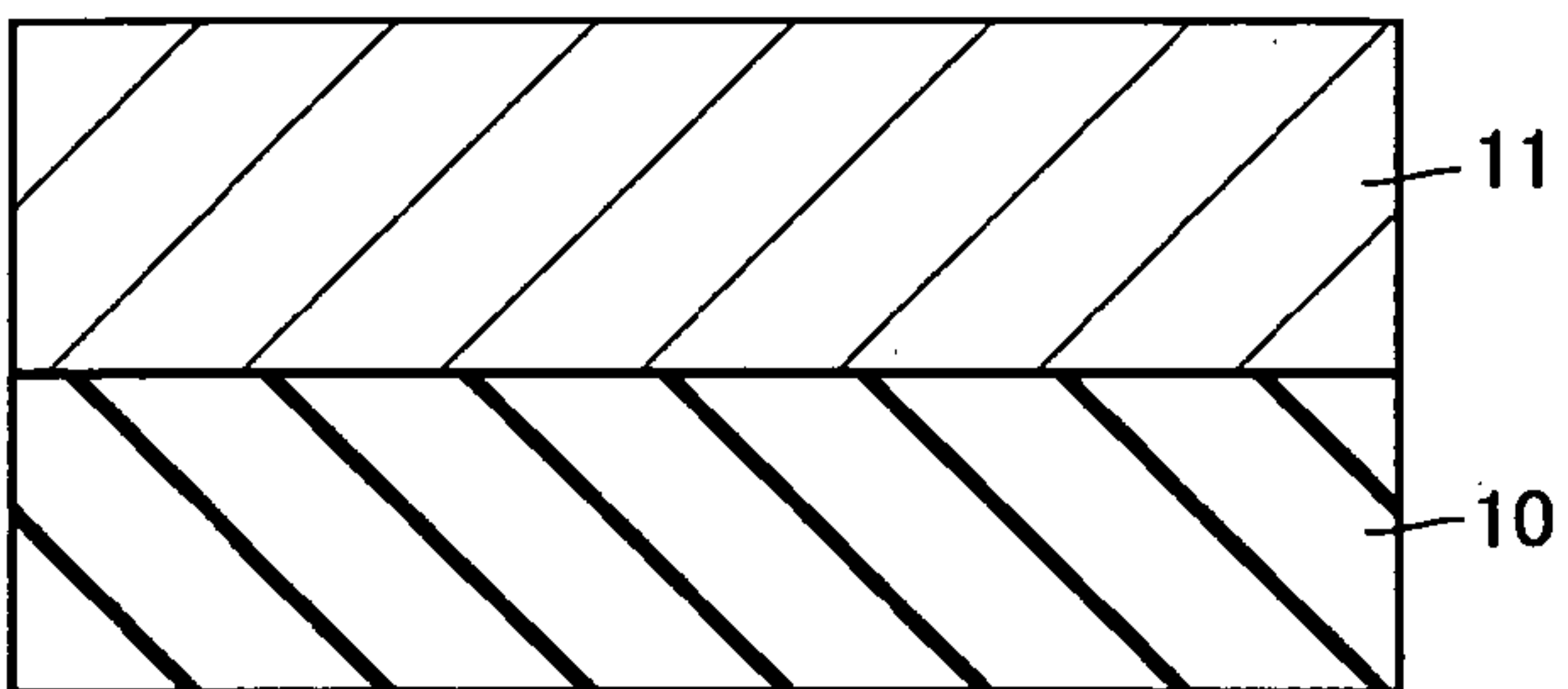


FIG.4C PRIOR ART

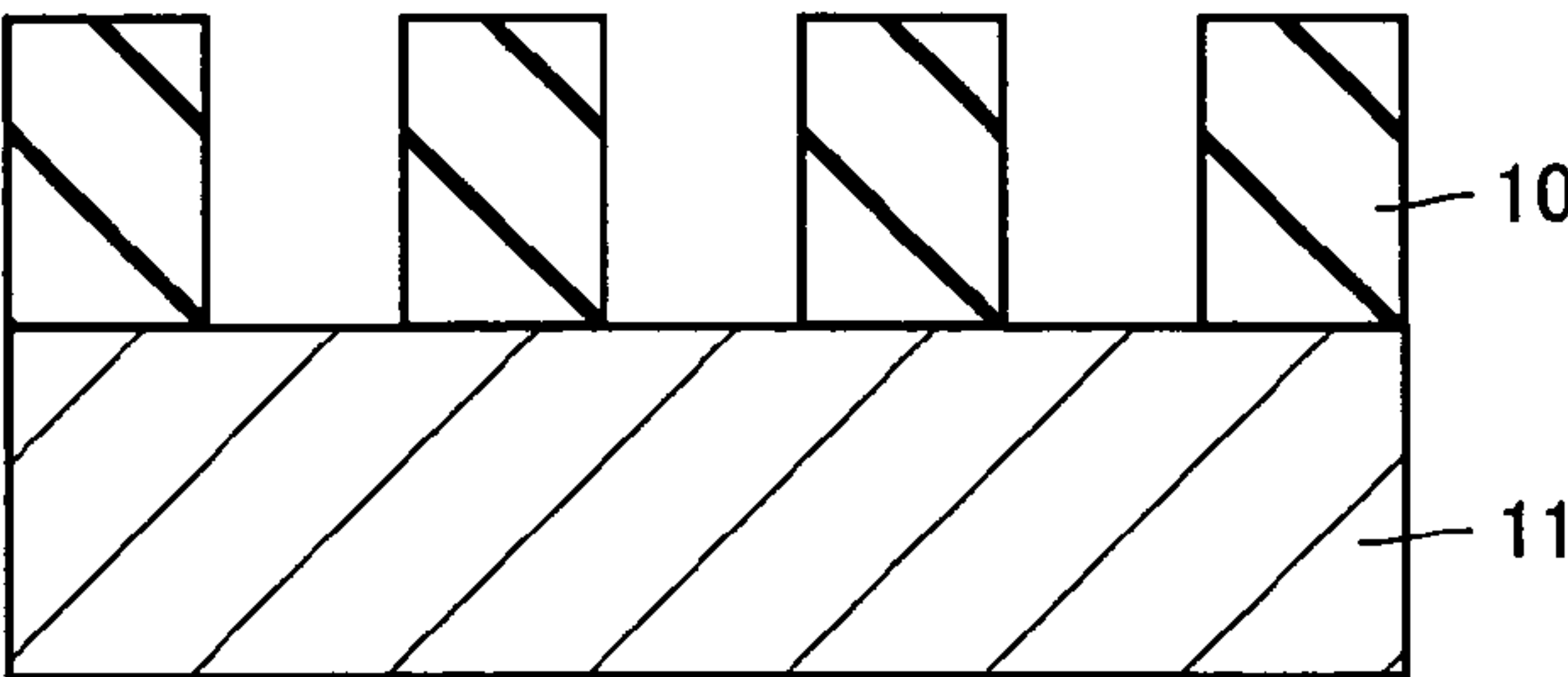


FIG.4D PRIOR ART

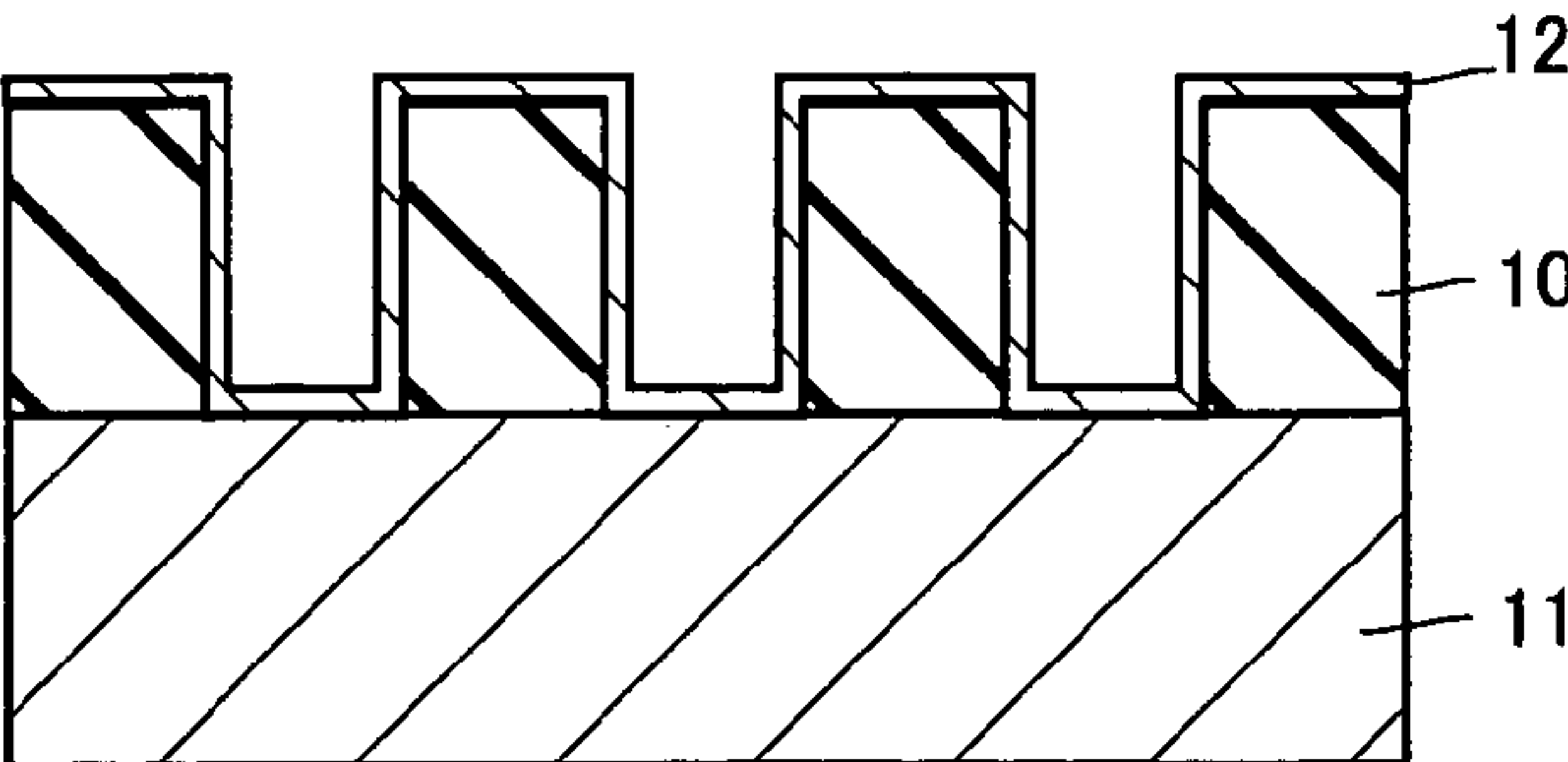




FIG.5A  
PRIOR ART

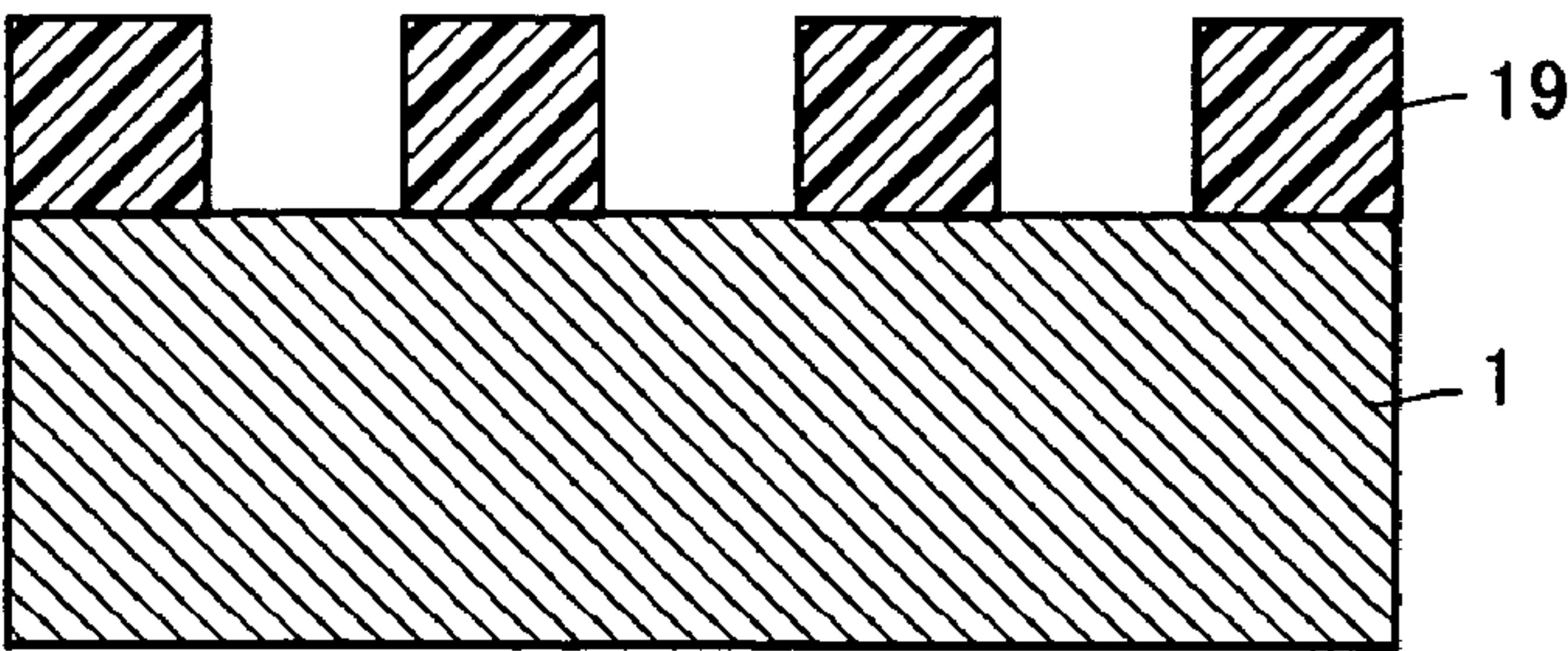


FIG.5B  
PRIOR ART

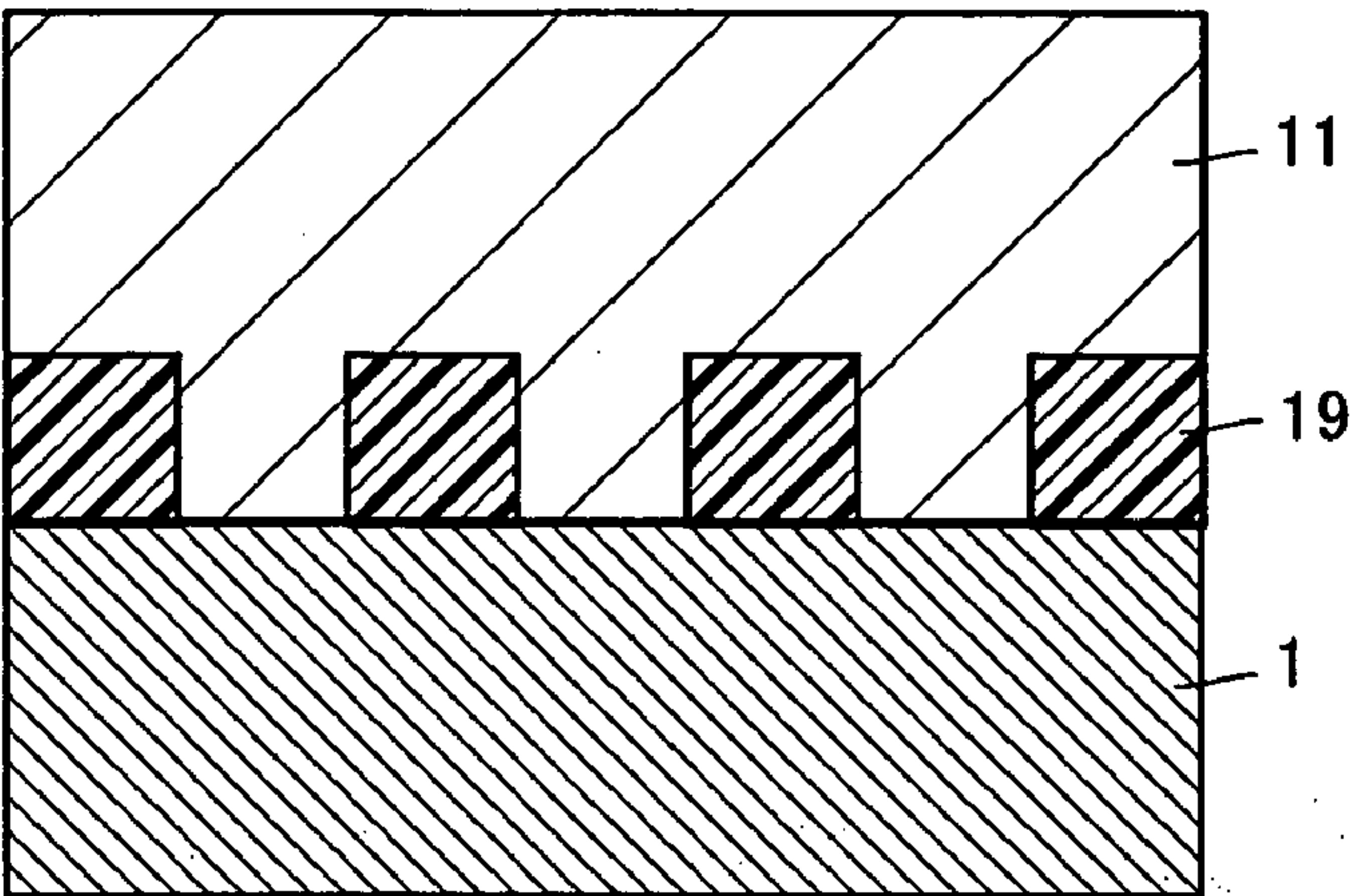


FIG.5C  
PRIOR ART

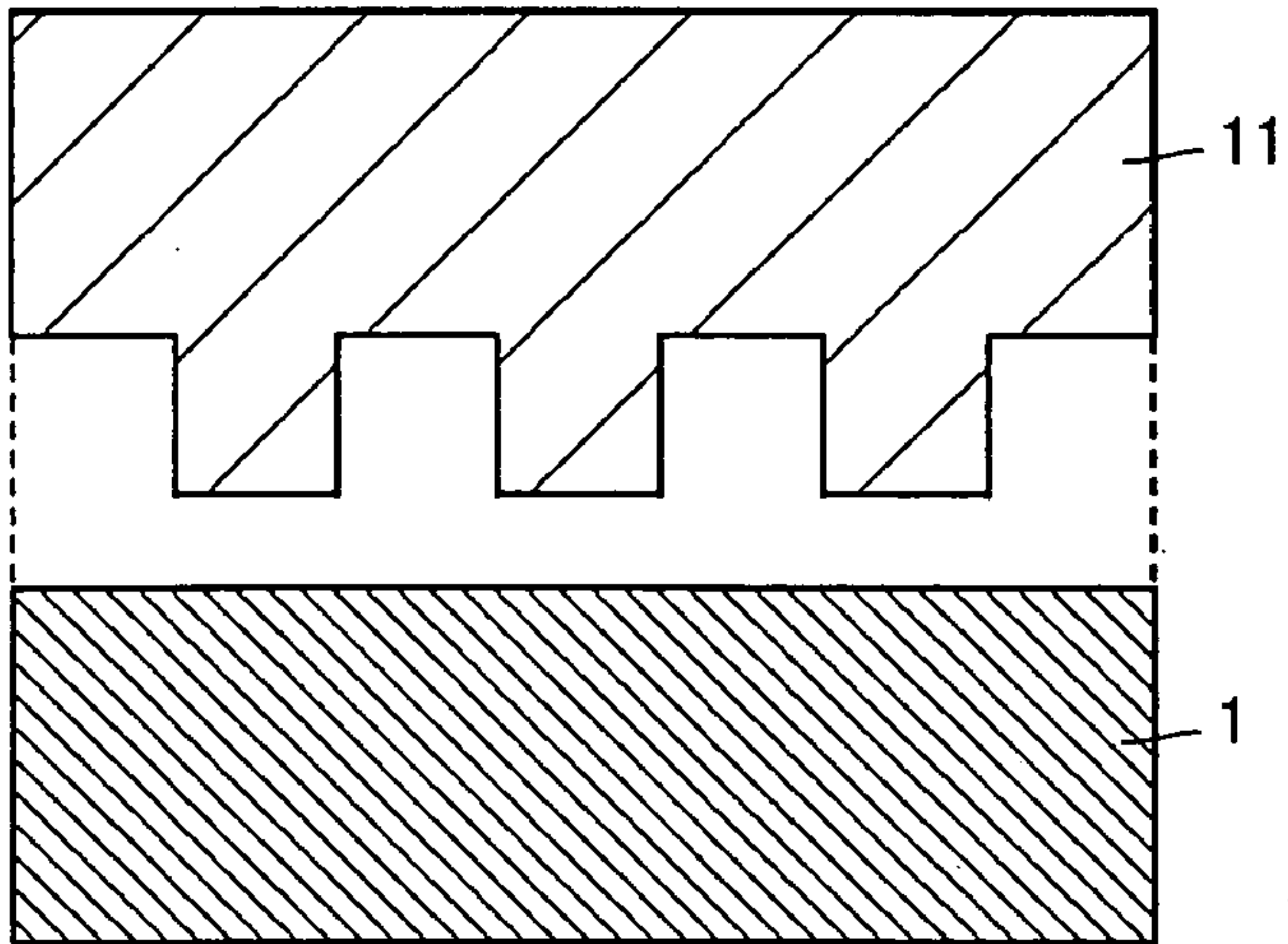
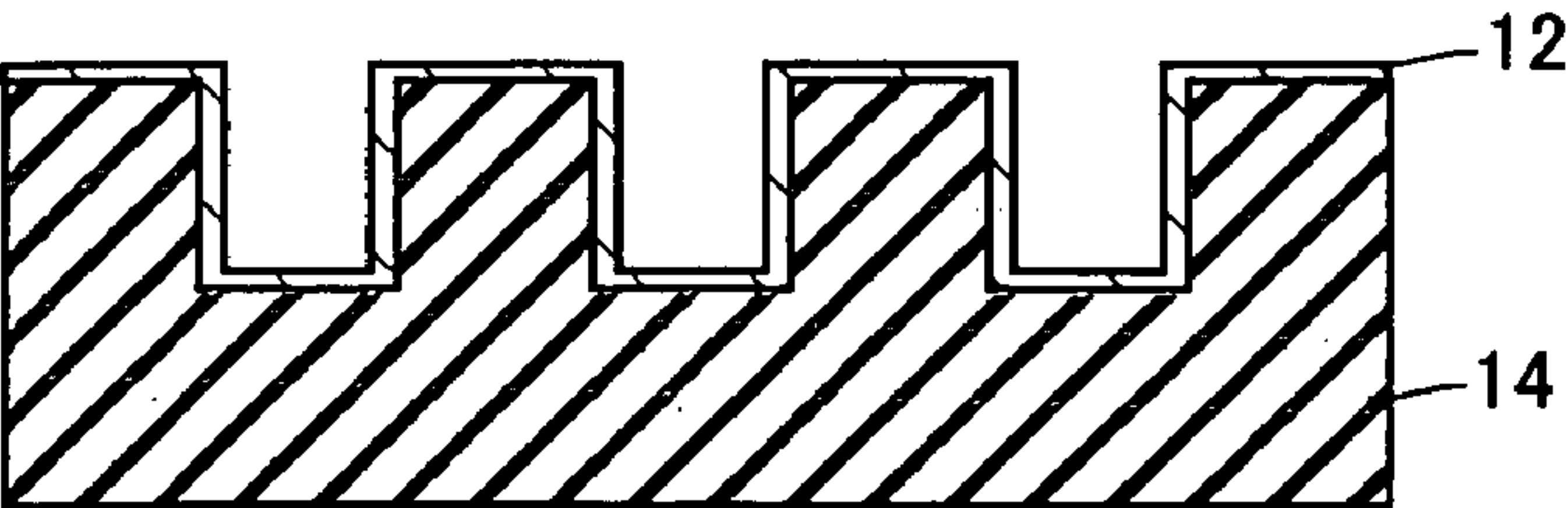


FIG.5D  
PRIOR ART





# MOLTEN SALT BATH FOR ELECTROFORMING AND METHOD OF MANUFACTURING METAL PRODUCT USING THE SAME

## BACKGROUND OF THE INVENTION

### [0001] 1. Field of the Invention

[0002] The present invention relates to a molten salt bath for electroforming and a method of manufacturing a metal product using the same, and more particularly to a molten salt bath for electroforming allowing electroforming at low temperature and a method of manufacturing a metal product using the same.

### [0003] 2. Description of the Background Art

[0004] Conventionally, an LiCl—KCl-based eutectic mixture obtained by mixing lithium chloride (LiCl) and potassium chloride (KCl) has generally been used as a molten salt bath for electroforming.

[0005] For example, 0.1 to 10 mass % of tungsten chloride ( $WCl_2$ ) with respect to the total mass of the molten salt bath for electroforming is added to the molten salt bath for electroforming prepared by mixing 45 mass % of LiCl and 55 mass % of KCl with respect to the total mass of the molten salt bath for electroforming. Then, a pair of electrodes consisting of an anode and a cathode is immersed into the molten salt bath for electroforming, and thereafter, a current of several A/dm<sup>2</sup> is fed between these electrodes in a heated state around 500° C. under an Argon (Ar) atmosphere. In this manner, tungsten (W) is precipitated on the surface of the cathode, thereby forming a metal product with a prescribed shape.

[0006] On the other hand, the LiCl—KCl-based molten salt bath for electroforming has a high melting point around 352° C., and accordingly, electroforming had to be performed at a temperature higher than that, for example, at approximately 500° C. as described above. If an electroforming mold having a resist pattern formed on the surface of a conductive substrate made of stainless or the like is used as the cathode, the resist consisting essentially of acrylic or the like is pyrolyzed, and the metal product in a prescribed shape cannot be obtained.

[0007] Then, for the molten salt bath for electroforming requiring a high temperature such as the LiCl—KCl-based molten salt bath, an electroforming mold obtained by silicon (Si) trench etching or an electroforming mold obtained by glass transfer may be employed as the cathode.

[0008] A method of manufacturing an electroforming mold using Si trench etching will now be described with reference to FIGS. 4A to 4D. It is noted that the same reference characters refer to the same or corresponding components in the figures.

[0009] First, as shown in FIG. 4A, a nickel (Ni) film 11 is formed on an Si substrate 10 by sputtering. Then, Ni is further precipitated on Ni film 11 by electroplating, so as to increase a thickness of Ni film 11, as shown in FIG. 4B. Thereafter, as shown in FIG. 4C, Si substrate 10 is subjected to trench etching, so as to pattern Si substrate 10 in a prescribed shape. Finally, as shown in FIG. 4D, a metal film 12 is vapor-deposited on the surface of exposed Ni film 11 and Si substrate 10. Thus, the electroforming mold is manufactured by using Si trench etching.

[0010] A method of manufacturing an electroforming mold using glass transfer will now be described with reference to FIGS. 5A to 5D. First, as shown in FIG. 5A, a resist 19 is patterned on the surface of conductive substrate 1 made of stainless or the like by SR lithography using synchrotron radiation (SR) light. Then, as shown in FIG. 5B, Ni film 11 is formed on conductive substrate 1 in a prescribed shape by electroforming. Thereafter, as shown in FIG. 5C, resist 19 is removed, and Ni film 11 is separated from conductive substrate 1. Finally, the shape of Ni film 11 is transferred onto a glass 14 as shown in FIG. 5D, and thereafter, metal film 12 is vapor-deposited on the surface of glass 14. In this manner, the electroforming mold is manufactured by using glass transfer.

[0011] In the electroforming mold obtained by Si trench etching, however, a stripe pattern caused by trench etching is formed. Accordingly, a similar stripe pattern is also formed on the surface of the metal product obtained by using the electroforming mold.

[0012] In addition, in the electroforming mold obtained by glass transfer, a metal precipitation surface of the electroforming mold is made coarse by repeating transfer for a plurality of times. Accordingly, the metal product obtained by using the electroforming mold has had poor accuracy.

[0013] Moreover, a number of process steps are required in manufacturing the electroforming molds as described above. Therefore, manufacturing the electroforming mold has been expensive.

## SUMMARY OF THE INVENTION

[0014] In view of the problems above, an object of the present invention is to provide a molten salt bath for electroforming allowing electroforming at low temperature and a method of manufacturing a metal product using the same.

[0015] According to the present invention, a molten salt bath for electroforming containing lithium bromide, cesium bromide, and a halide of an alkali metal and/or a halide of an alkaline-earth metal is provided. Here, it is considered that a substance contained in the molten salt bath for electroforming according to the present invention is at least partially ionized in the molten salt bath for electroforming.

[0016] Preferably, in the molten salt bath for electroforming according to the present invention, the halide of the alkali metal is potassium bromide.

[0017] In addition, preferably in the molten salt bath for electroforming according to the present invention, the sum of a mole fraction of lithium bromide and a mole fraction of cesium bromide is set to be within a range from at least 0.5 to less than 0.95 with respect to the entire molten salt bath for electroforming.

[0018] Further, preferably in the molten salt bath for electroforming according to the present invention, a mole ratio of lithium bromide to cesium bromide (lithium bromide/cesium bromide) is set to be within a range from at least 1.8 to at most 2.5.

[0019] Preferably, the molten salt bath for electroforming according to the present invention has a eutectic composition.



[0020] In addition, according to the present invention, a method of manufacturing a metal product including the steps of: forming a resist pattern on a conductive substrate and exposing a portion of the conductive substrate; immersing the conductive substrate having the resist pattern formed into the molten salt bath for electroforming described above, the molten salt bath for electroforming containing a metal to be precipitated and/or a compound of a metal to be precipitated; and precipitating the metal at a portion where the conductive substrate is exposed, is provided.

[0021] In the method of manufacturing a metal product according to the present invention, preferably, a temperature of the molten salt bath for electroforming is set to at most 300° C. in precipitating the metal.

[0022] Further according to the present invention, a molten salt bath for electroforming is obtained by mixing lithium bromide, cesium bromide, and a halide of an alkali metal and/or a halide of an alkaline-earth metal.

[0023] The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0024] FIGS. 1A to 1C are schematic cross-sectional views of a conductive substrate used in the present invention.

[0025] FIG. 2 is a perspective side view schematically showing one example of an electroforming apparatus used in the present invention.

[0026] FIG. 3 is a schematic perspective side view of an experimental apparatus used in Examples.

[0027] FIGS. 4A to 4D are schematic cross-sectional views showing a flow in manufacturing an electroforming mold using conventional Si trench etching.

[0028] FIGS. 5A to 5D are schematic cross-sectional views showing a flow in manufacturing an electroforming mold using conventional glass transfer.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0029] (Molten Salt Bath for Electroforming)

[0030] According to the present invention, a molten salt bath for electroforming containing lithium bromide (LiBr), cesium bromide (CsBr), and a halide of an alkali metal and/or a halide of an alkaline-earth metal is provided. Here, a bromide instead of a chloride such as a conventional LiCl—KCl-based substance is mixed so that the molten salt bath for electroforming contains anions having a larger size as well as cations ( $\text{Li}^+$ ,  $\text{Cs}^+$ ) having a size different from each other, thereby lowering affinity between anions and cations. In addition, by mixing three or more halides, the melting point of the molten salt composing the molten salt bath for electroforming is lowered. The molten salt bath for electroforming allowing electroforming at low temperature has been completed from such a technical concept. Though the molten salt bath for electroforming consisting essentially of iodides is assumed to allow electroforming at further lower temperature, the molten salt bath for electroforming has become unstable and actual electroforming could not be performed.

[0031] When the molten salt bath for electroforming is used, electroforming can be performed at a low temperature, for example, in a range from at least 230° C. to at most 300° C. Accordingly, electroforming can be performed at a temperature at which the resist is not pyrolyzed. Therefore, instead of the electroforming mold obtained through conventional complex process steps, an electroforming mold solely having a resist pattern formed on the conductive substrate made of stainless or the like, that is, readily fabricated, is employed, so as to manufacture with high accuracy a metal product composed of a metal with high melting point and high strength such as chromium (Cr), tungsten (W) or titanium (Ti).

[0032] The molten salt bath for electroforming can be obtained by melting and mixing LiBr powder, CsBr powder, and powder of the halide of the alkali metal and/or powder of the halide of the alkaline-earth metal. It is to be noted that the molten salt bath for electroforming according to the present invention may contain other substances such as an oxide which is inevitably produced.

[0033] Examples of the halides of the alkali metal other than LiBr and CsBr include lithium fluoride (LiF), lithium chloride (LiCl), lithium iodide (LiI), sodium fluoride (NaF), sodium chloride (NaCl), sodium bromide (NaBr), sodium iodide (NaI), potassium fluoride (KF), potassium chloride (KCl), potassium bromide (KBr), potassium iodide (KI), rubidium fluoride (RbF), rubidium chloride (RbCl), rubidium bromide (RbBr), rubidium iodide (RbI), cesium fluoride (CsF), cesium chloride (CsCl), or cesium iodide (CsI).

[0034] Examples of the halides of the alkaline-earth metal include magnesium fluoride ( $\text{MgF}_2$ ), magnesium chloride ( $\text{MgCl}_2$ ), magnesium bromide ( $\text{MgBr}_2$ ), magnesium iodide ( $\text{MgI}_2$ ), calcium fluoride ( $\text{CaF}_2$ ), calcium chloride ( $\text{CaCl}_2$ ), calcium bromide ( $\text{CaBr}_2$ ), calcium iodide ( $\text{CaI}_2$ ), strontium fluoride ( $\text{SrF}_2$ ), strontium chloride ( $\text{SrCl}_2$ ), strontium bromide ( $\text{SrBr}_2$ ), strontium iodide ( $\text{SrI}_2$ ), barium fluoride ( $\text{BaF}_2$ ), barium chloride ( $\text{BaCl}_2$ ), barium bromide ( $\text{BaBr}_2$ ), or barium iodide ( $\text{BaI}_2$ ).

[0035] Among others, KBr is preferably mixed as a halide of the alkali metal. In this case, cations ( $\text{K}^+$ ) of the alkali metal having a size intermediate between that of  $\text{Li}^+$  and  $\text{Cs}^+$  can further be contained in the molten salt bath for electroforming. Therefore, affinity between the cation and the anion in the molten salt bath for electroforming can further be lowered. In particular, when the molten salt bath for electroforming obtained by mixing LiBr, CsBr and KBr is used, electroforming at further low temperature can be performed. Here, at least one of the halide of the alkali metal and the halide of the alkaline-earth metal should only be contained. In addition, one type or two or more types of the halides may be contained.

[0036] Preferably, mixing is performed such that the sum of the mole fraction of LiBr and the mole fraction of CsBr is set to be within a range from at least 0.5 to less than 0.95 with respect to the entire molten salt bath for electroforming having an amount of substance of 1. If the sum of the mole fractions is less than 0.5, an effect to lower the affinity between the anion and the cation by containing anions having a larger size and cations ( $\text{Li}^+$ ,  $\text{Cs}^+$ ) having different sizes in the molten salt bath for electroforming cannot sufficiently be attained. On the other hand, if the sum of the mole fractions is 0.95 or over, an effect to lower the melting point of the molten salt composing the molten salt bath for electroforming by mixing a halide other than LiBr and CsBr cannot sufficiently be attained.



[0037] Moreover, preferably, mixing is performed such that the mole ratio of LiBr to CsBr (LiBr/CsBr) is set to be within a range from at least 1.8 to at most 2.5. If the mole ratio (LiBr/CsBr) is less than 1.8, too many cations ( $\text{Cs}^+$ ) having a larger size tend to be present in the molten salt bath for electroforming. Accordingly, an effect to lower the affinity between the anion and the cation by containing cations having different sizes cannot sufficiently be attained. On the other hand, if the mole ratio (LiBr/CsBr) is over 2.5, too many cations ( $\text{Li}^+$ ) having a smaller size tend to be present in the molten salt bath for electroforming. Accordingly, an effect to lower the affinity between the anion and the cation by containing cations having different sizes cannot sufficiently be attained.

[0038] Furthermore, preferably, LiBr, CsBr, and the halide of the alkali metal and/or the halide of the alkaline-earth metal are mixed such that the molten salt bath for electroforming has a eutectic composition. In this case, as the molten salt bath for electroforming can be prepared at a eutectic point, electroforming can be performed at a temperature in the vicinity of a eutectic temperature.

[0039] From the viewpoint of the technical concept described above, the molten salt bath for electroforming according to the present invention can have at least ternary composition, for example: LiBr—CsBr—KBr, LiBr—CsBr—LiF, LiBr—CsBr—LiCl, LiBr—CsBr—LiI, LiBr—CsBr—NaF, LiBr—CsBr—NaCl, LiBr—CsBr—NaBr, LiBr—CsBr—NaI, LiBr—CsBr—KF, LiBr—CsBr—KCl, LiBr—CsBr—KI, LiBr—CsBr—RbF, LiBr—CsBr—RbCl, LiBr—CsBr—RbBr, LiBr—CsBr—RbI, LiBr—CsBr—CsF, LiBr—CsBr—CsCl, LiBr—CsBr—CsI, LiBr—CsBr—MgF<sub>2</sub>, LiBr—CsBr—MgCl<sub>2</sub>, LiBr—CsBr—MgBr<sub>2</sub>, LiBr—CsBr—MgI<sub>2</sub>, LiBr—CsBr—CaF<sub>2</sub>, LiBr—CsBr—CaCl<sub>2</sub>, LiBr—CsBr—CaBr<sub>2</sub>, LiBr—CsBr—CaI<sub>2</sub>, LiBr—CsBr—SrF<sub>2</sub>, LiBr—CsBr—SrCl<sub>2</sub>, LiBr—CsBr—SrBr<sub>2</sub>, LiBr—CsBr—SrI<sub>2</sub>, LiBr—CsBr—BaF<sub>2</sub>, LiBr—CsBr—BaCl<sub>2</sub>, LiBr—CsBr—BaBr<sub>2</sub>, LiBr—CsBr—BaI<sub>2</sub>, LiBr—CsBr—KBr—LiF, LiBr—CsBr—KBr—LiCl, LiBr—CsBr—KBr—LiI, LiBr—CsBr—KBr—NaF, LiBr—CsBr—KBr—NaCl, LiBr—CsBr—KBr—NaBr, LiBr—CsBr—KBr—NaI, LiBr—CsBr—KBr—KF, LiBr—CsBr—KBr—KCl, LiBr—CsBr—KBr—KI, LiBr—CsBr—KBr—RbF, LiBr—CsBr—KBr—RbCl, LiBr—CsBr—KBr—RbBr, LiBr—CsBr—KBr—RbI, LiBr—CsBr—KBr—CsF, LiBr—CsBr—KBr—CsCl, LiBr—CsBr—KBr—CsI, LiBr—CsBr—KBr—MgF<sub>2</sub>, LiBr—CsBr—KBr—MgCl<sub>2</sub>, LiBr—CsBr—KBr—MgBr<sub>2</sub>, LiBr—CsBr—KBr—MgI<sub>2</sub>, LiBr—CsBr—KBr—CaF<sub>2</sub>, LiBr—CsBr—KBr—CaCl<sub>2</sub>, LiBr—CsBr—KBr—CaBr<sub>2</sub>, LiBr—CsBr—KBr—CaI<sub>2</sub>, LiBr—CsBr—KBr—SrF<sub>2</sub>, LiBr—CsBr—KBr—SrCl<sub>2</sub>, LiBr—CsBr—KBr—SrBr<sub>2</sub>, LiBr—CsBr—KBr—SrI<sub>2</sub>, LiBr—CsBr—KBr—BaF<sub>2</sub>, LiBr—CsBr—KBr—BaCl<sub>2</sub>, LiBr—CsBr—KBr—BaBr<sub>2</sub>, or LiBr—CsBr—KBr—BaI<sub>2</sub>. It is to be noted that notation such as LiBr—CsBr—MX in the description above means that LiBr, CsBr and MX are mixed to compose the molten salt bath for electroforming according to the present invention.

[0040] (Method of Manufacturing Metal Product)

[0041] In the following, a preferred example of a method of manufacturing a metal product according to the present invention will be described with reference to the figures.

[0042] First, referring to FIG. 1A, conductive substrate 1 made, for example, of stainless, copper (Cu), iron (Fe),

nickel (Ni), or the like is prepared. Then, referring to FIG. 1B, resist 2 is applied to conductive substrate 1 and irradiated with UV (ultraviolet) light or SR light. Here, a UV resist or the like used as resist 2 if UV light is used for irradiating resist 2, and PMMA (polymethylmethacrylate) or the like is used as resist 2 if SR light is used for irradiation.

[0043] Then, referring to FIG. 1C, a portion except for resist 2 irradiated with the UV light or the SR light is removed to form a resist pattern on conductive substrate 1, and the surface of conductive substrate 1 is partially exposed. Electroforming mold 3 is thus formed. In the present invention, electroforming mold 3 formed with such a simplified method can be employed.

[0044] Such electroforming mold 3 is placed as a cathode in an electroforming apparatus 4 shown in the schematic perspective side view in FIG. 2, for example, so as to perform electroforming. Referring to FIG. 2, electroforming apparatus 4 including a stainless holder 5, a cover 6 capable of sealing stainless holder 5, an anode 7, a crucible 8 made of high-purity alumina, a reference electrode 13, and a thermocouple 15 for measuring a temperature is placed in a globe box (not shown) under an Ar atmosphere.

[0045] Molten salt bath for electroforming 9 obtained by melting and mixing LiBr powder, CsBr powder and the like is placed in crucible 8. Here, molten salt bath for electroforming 9 contains a metal to be precipitated and/or a compound of the metal to be precipitated in electroforming mold 3. A metal with high melting point and high strength such as Cr, W or Ti is suitably used as the metal to be precipitated in electroforming mold 3. If such a metal is added in a solution and electroforming is performed, H<sub>2</sub> is produced at the cathode in an amount larger than the metal, because a reduction potential of such a metal is lower (basier) than that of hydrogen in the entire pH range. Accordingly, if a sufficiently low (base) potential initiating precipitation of a metal is applied, H<sub>2</sub> is produced in a large amount, and it is extremely difficult to precipitate a metal in a film shape. If molten salt bath for electroforming 9 according to the present invention is used, however, the metal such as Cr, W or Ti has a reduction potential lower (basier) than that of the alkali metal and the alkaline-earth metal, and therefore, such a metal can be precipitated at the cathode. Here, examples of the compound of the metal to be precipitated include tungsten chloride (WCl<sub>2</sub>), chromium chloride (CrCl<sub>2</sub>), titanium chloride (TiCl<sub>2</sub>), tungsten bromide (WBr<sub>2</sub>), chromium bromide (CrBr<sub>2</sub>), tungsten fluoride (WF<sub>2</sub>), and chromium fluoride (CrF<sub>2</sub>).

[0046] Electroforming is performed in a state in which molten salt bath for electroforming 9 is heated to approximately 200 to 300° C. Here, if a current having current density of not smaller than 1 mA/cm<sup>2</sup> to not larger than 500 mA/cm<sup>2</sup>, preferably not smaller than 10 mA/cm<sup>2</sup> to not larger than 500 mA/cm<sup>2</sup>, and further preferably not smaller than 50 mA/cm<sup>2</sup> to not larger than 500 mA/cm<sup>2</sup> is fed between anode 7 and electroforming mold 3 serving as the cathode, the metal described above is precipitated on the surface of electroforming mold 3 serving as the cathode, thereby forming a metal product having a prescribed shape.

[0047] In other words, if a current having a current density in the above-described range is fed, a metal product with higher hardness can be formed in a shorter period of time.

[0048] After electroforming is completed, electroforming mold 3 is taken out from molten salt bath for electroforming



**9** and washed with water. Then, a desired metal product is separated from electroforming mold **3**, and resist **2** adhered to the separated metal product is removed, for example, by ashing. Thus, a metal product having a prescribed shape is obtained.

[0049] As described above, in the present invention, the temperature of molten salt bath for electroforming **9** in precipitation of the metal is set to not larger than 300° C. Therefore, even if electroforming mold **3** is immersed in molten salt bath for electroforming **9**, resist **2** formed on electroforming mold **3** is not pyrolyzed. Since electroforming mold **3** solely having resist **2** formed on conductive substrate **1** can be employed, a metal product with high accuracy can be obtained with further lower cost.

[0050] (Application)

[0051] The molten salt bath for electroforming and the method of manufacturing a metal product using the same according to the present invention have characteristics as described above. Therefore, the molten salt bath for electroforming and the method are suitably used for manufacturing a metal product having a Vickers hardness (HV) of not smaller than 600 to not larger than 2000 (a metal mold, for example).

## EXAMPLES

### Examples 1 to 9

[0052] In crucible **8** in an experimental apparatus **18** shown in the schematic perspective side view in FIG. 3, molten salt baths for electroforming **9** in Examples 1 to 9 having compositions shown in Table 1 were prepared. Then, CrCl<sub>2</sub> was added to each molten salt bath for electroforming in such an amount that the mole fraction thereof attains 0.01 with respect to the entire molten salt bath for electroforming. Thereafter, in a state in which the temperatures of respective molten salt baths for electroforming **9** in Examples 1 to 9 were set to 250° C. or 300° C., a current of 10 mA/cm<sup>2</sup>, 50 mA/cm<sup>2</sup> or 100 mA/cm<sup>2</sup> was fed between a Cr plate **17** and an Ni plate **16** in experimental apparatus **18** for 10 minutes. States of Cr precipitated on Ni plate **16** were evaluated with visual inspection and with an optical microscope, based on a standard described below. Evaluation results are shown in Table 1. Note that the experiment was conducted in the globe box under the Ar atmosphere.

[0053] Standard of Evaluation

[0054] A . . . Extremely good precipitation and metallic luster were observed.

[0055] B . . . Good precipitation and metallic luster were observed.

[0056] C . . . Precipitation was observed, however, smoothness was insufficient. No metallic luster was observed.

[0057] D . . . Almost no precipitation was observed.

[0058] Consequently, as shown in Table 1, in Examples 2 to 4 and Examples 6 to 9 where the sum of the mole fraction of LiBr and the mole fraction of CsBr is in a range from at least 0.5 to less than 0.95 with respect to the entire molten salt bath for electroforming, the precipitation state of Cr at 250° C. and 300° C. was better than that in Example 1 (0.45) and Example 5 (0.97) where the sum of the mole fractions was not in the above-described range. Examples 2 to 4 and Examples 6 to 9 were found to be more suitable as the molten salt bath for electroforming.

[0059] In addition, in Examples 2 to 4 and Examples 7 to 8 where the sum of the mole fraction of LiBr and the mole fraction of CsBr is in a range from at least 0.5 to less than 0.95 with respect to the entire molten salt bath for electroforming and the mole ratio of LiBr to CsBr is in a range from at least 1.8 to at most 2.5, the precipitation state of Cr when the current of 100 mA/cm<sup>2</sup> was fed was better than that in Example 6 (1.6) and Example 9 (2.7) where the mole ratio (LiBr/CsBr) was not in the above-described range. Examples 2 to 4 and Examples 7 to 8 were found to be more suitable as the molten salt bath for electroforming.

[0060] Moreover, in Example 3 having the eutectic composition (having mole ratio of LiBr:CsBr:KBr=56.1:25:18.9), the precipitation state of Cr was considerably better than that in other Examples not having the eutectic composition (Examples 1 to 2 and 4 to 9) not only at 300° C. but also at a low temperature of 250° C. Example 3 was found to be considerably suitable as the molten salt bath for electroforming at low temperature.

### Example 10

[0061] A photoresist having a thickness of 50 μm consisting of PMMA was applied on the surface of an Ni substrate

TABLE 1

Composition Ratio							Cr Precipitation State					
							250° C.			300° C.		
							10	50	100	10	50	100
Composition			(mol)									
1	2	3	1:2:3	1 + 2/total	1/2	(mA/cm <sup>2</sup> )	(mA/cm <sup>2</sup> )	(mA/cm <sup>2</sup> )	(mA/cm <sup>2</sup> )	(mA/cm <sup>2</sup> )	(mA/cm <sup>2</sup> )	
Example 1	LiBr	CsBr	KBr	31.1:13.9:55.0	0.45	2.24	C	C	C	B	C	C
Example 2	LiBr	CsBr	KBr	34.6:15.4:50.0	0.50	2.24	B	B	B	B	B	B
Example 3	LiBr	CsBr	KBr	56.1:25.0:18.9	0.811	2.24	A	A	A	A	A	A
Example 4	LiBr	CsBr	KBr	65.7:29.2:5.1	0.949	2.24	B	B	B	B	B	B
Example 5	LiBr	CsBr	KBr	67.1:29.9:3.0	0.97	2.24	C	C	C	B	C	C
Example 6	LiBr	CsBr	KBr	49.9:31.2:18.9	0.811	1.6	B	B	C	B	B	C
Example 7	LiBr	CsBr	KBr	52.1:29.0:18.9	0.811	1.8	B	B	B	B	B	B
Example 8	LiBr	CsBr	KBr	57.9:23.2:18.9	0.811	2.5	B	B	B	B	B	B
Example 9	LiBr	CsBr	KBr	59.2:21.9:18.9	0.811	2.7	B	B	C	B	B	C



in a square shape having a side of 1 cm. The photoresist was irradiated with SR light, and the resist in an area other than the area irradiated with the SR light was removed. A resist pattern in a grid having a line/space of  $50\ \mu\text{m}/50\ \mu\text{m}$  was thus formed on the Ni substrate.

[0062] The Ni substrate was immersed as electroforming mold **3** in 500 grams of molten salt bath for electroforming **9** placed in crucible **8** in electroforming apparatus **4** shown in FIG. 2. Here, molten salt bath for electroforming **9** is composed of LiBr, CsBr and KBr (mole ratio of LiBr:CsBr:KBr=56.1:25:18.9).  $\text{CrCl}_2$  was added to molten salt bath for electroforming **9** in such an amount that the mole fraction thereof attains 0.01 with respect to the entire molten salt bath for electroforming **9**.

[0063] Then, a current having a current density of  $100\ \text{mA}/\text{cm}^2$  was fed between anode **7** composed of Cr and electroforming mold **3** for 50 minutes in a state where the temperature of molten salt bath for electroforming **9** was set to  $250^\circ\text{C}$ . Thereafter, an amount of the current was doubled, and the current of doubled amount was fed for further 200 minutes. In this manner, an electroformed product composed of Cr was obtained on electroforming mold **3**. Here, an electrode potential at the cathode with respect to reference electrode **13** during electroforming gradually increased from  $-0.90\text{V}$ , and attained to  $-0.80\text{V}$  30 minutes later. Then, immediately after the current amount was doubled, the electrode potential fell to  $-0.93\text{V}$ , and thereafter rose again to attain  $-0.79\text{V}$  at completion of electroforming.

[0064] Thereafter, electroforming mold **3** was taken out from electroforming apparatus **4** and washed with water, whereby salt adhered to the electroformed product composed of Cr was removed. Then, after electroforming mold **3** and the electroformed product were dried, the surface of the electroformed product was polished in order to improve smoothness and to adjust thickness thereof to  $200\ \mu\text{m}$ .

[0065] Finally, a resin adhered to the electroformed product mechanically separated from electroforming mold **3** was removed with plasma ashing, and a metal product composed of Cr and having convex portions formed in a grid and concave portions arranged in a grid between protrusions was obtained.

[0066] Thus obtained metal product composed of Cr had a Vickers hardness (HV) of 800. Here, the metal product in Example 10 was also manufactured in the globe box under the Ar atmosphere.

#### Comparative Example 1

[0067] A metal product composed of Cr was obtained in the same manner as in Example 10, except that molten salt bath for electroforming **9** composed of LiCl and KCl (having a mass ratio of LiCl:KCl=45:55) was used to perform electroforming at a high temperature of  $400^\circ\text{C}$ . Here, the electrode potential at the cathode with respect to reference electrode **13** during electroforming gradually increased from  $-0.85\text{V}$ , and attained to  $-0.76\text{V}$  30 minutes later. Then, immediately after the current amount was doubled, the electrode potential fell to  $-0.90\text{V}$ , and thereafter rose again to attain  $-0.75\text{V}$  at completion of electroforming.

[0068] When the metal product composed of Cr obtained in Comparative Example 1 was observed with an SEM

(scanning electron microscope), it was found that the resist pattern was not transferred to this metal product. This may be because the resist on electroforming mold **3** deformed during electroforming due to the high temperature at  $400^\circ\text{C}$ .

[0069] As described above, according to the present invention, a molten salt bath for electroforming allowing electroforming at low temperature and a method of manufacturing a metal product using the same can be provided.

[0070] Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of the present invention being limited only by the terms of the appended claims.

What is claimed is:

1. A molten salt bath for electroforming, containing lithium bromide, cesium bromide, and a halide of an alkali metal and/or a halide of an alkaline-earth metal.

2. The molten salt bath for electroforming according to claim 1, wherein

said halide of the alkali metal is potassium bromide.

3. The molten salt bath for electroforming according to claim 1, wherein

a sum of a mole fraction of said lithium bromide and a mole fraction of said cesium bromide is set to be within a range from at least 0.5 to less than 0.95 with respect to entire said molten salt bath for electroforming.

4. The molten salt bath for electroforming according to claim 1, wherein

a mole ratio of said lithium bromide to said cesium bromide (lithium bromide/cesium bromide) is set to be within a range from at least 1.8 to at most 2.5.

5. The molten salt bath for electroforming according to claim 1, wherein

said molten salt bath for electroforming has a eutectic composition.

6. A method of manufacturing a metal product, comprising the steps of:

forming a resist pattern on a conductive substrate and exposing a portion of said conductive substrate;

immersing said conductive substrate having said resist pattern formed into the molten salt bath for electroforming according to claim 1, the molten salt bath for electroforming containing a metal to be precipitated and/or a compound of a metal to be precipitated; and

precipitating said metal at a portion where said conductive substrate is exposed.

7. The method of manufacturing a metal product according to claim 6, wherein

a temperature of said molten salt bath for electroforming is set to at most  $300^\circ\text{C}$ . in precipitating said metal.

8. A molten salt bath for electroforming, obtained by mixing lithium bromide, cesium bromide, and a halide of an alkali metal and/or a halide of an alkaline-earth metal.