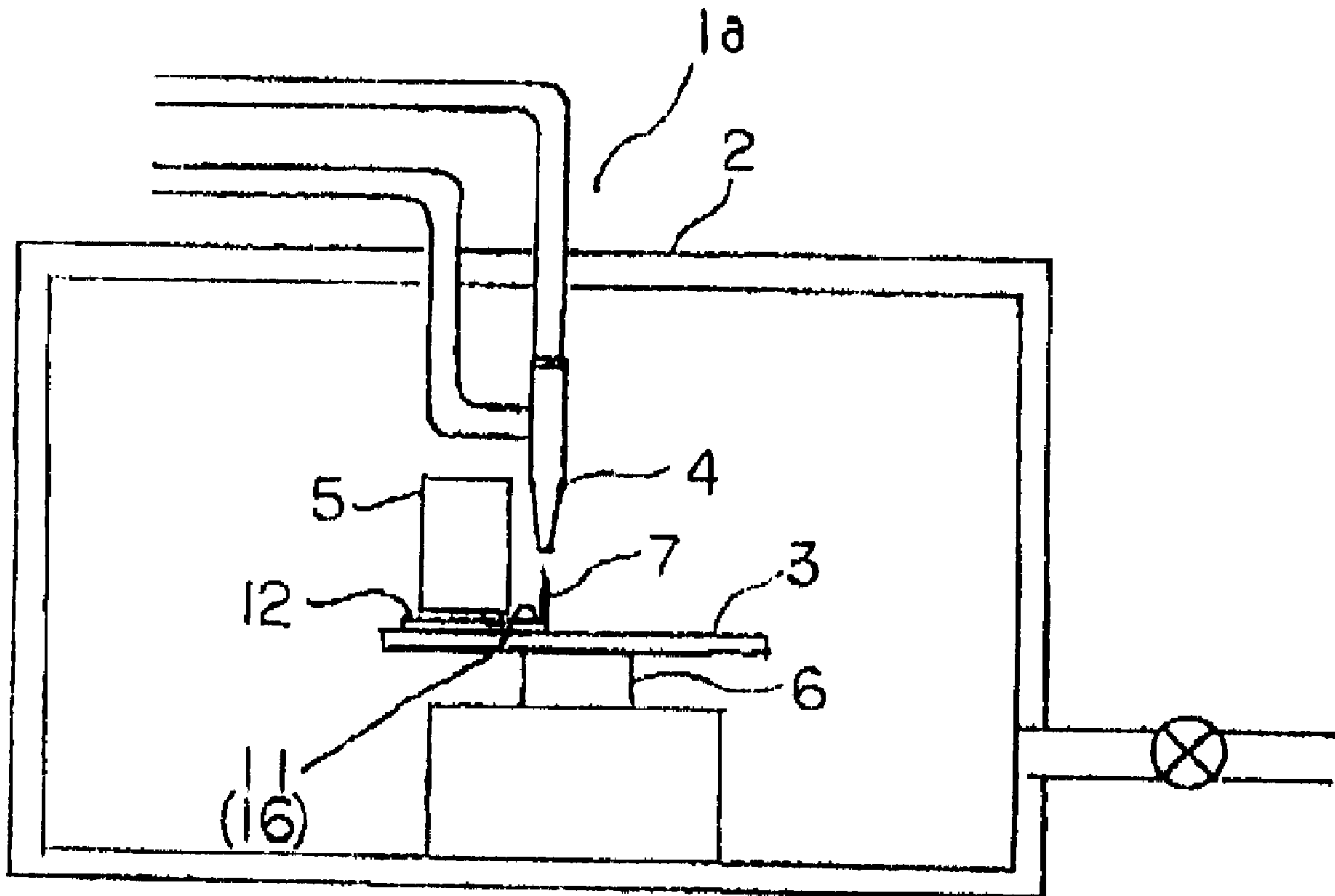




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(54) Titre : METHODE DE FORMATION A BASSE TEMPERATURE D'UNE STRUCTURE A PARTIR DE PARTICULES
 FRAGILES ULTRA-FINES
 (54) Title: METHOD OF FORMING SHAPED BODY OF BRITTLE ULTRA FINE PARTICLE AT LOW TEMPERATURE



(57) Abrégé/Abstract:

Disclosed is a method of forming a film or a microstructure having high density and high strength by bonding brittle ultrafine particles without heating them. The brittle ultrafine particles are blown onto a substrate, and then subjected to a mechanical impact force in order to first break the particles, then bond the ultrafine particles together, thus forming a film or microstructure on the substrate.

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Abstract

Disclosed is a method of forming a film or a microstructure having high density and high strength by bonding brittle ultrafine particles without heating them.

5 The brittle ultrafine particles are blown onto a substrate, and then subjected to a mechanical impact force in order to first break the particles, then bond the ultrafine particles together, thus forming a film or microstructure on the substrate.

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METHOD OF FORMING SHAPED BODY OF BRITTLE ULTRAFINE PARTICLE
AT LOW TEMPERATURE

BACKGROUND OF THE INVENTION

1. Field of the Invention

5 The present invention relates to techniques of forming a shaped body such as a film or a microstructure on a substrate by applying ultrafine particles of a brittle material such as ceramics to the substrate.

2. Description of the Related Art

10 As a technique for forming a film or a microstructure on a substrate by using ultrafine particles of a brittle material such as ceramics, a method of forming a film or a microstructure by mixing brittle ultrafine particles with a carrier gas and blowing the gas toward a
15 substrate via a fine nozzle has been proposed. In order to provide desired physical properties of the film or microstructure, it is essential that ultrafine particles in the film or microstructure have a desired bonding strength.

In practice, however, whether ultrafine particles
20 can be bonded and molded at high density and strength at room temperature without any thermal assistance depends on the physical properties of ultrafine particles to be used, and the reason of this is not still clear. Therefore, in order to obtain sufficient physical properties (mechanical
25 and electrical characteristics and the like) by using a conventional molding (film forming) method, it is usually required to heat a substrate to a temperature of several hundred degrees celsius or higher and thereafter bake it at a high temperature near the sintering temperature of
30 ceramics (brittle material). In general sintering

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techniques for ceramics, it is also essential to bake the ceramic material at a high temperature (at least 900°C or higher) in order to bond ultrafine particles by utilizing thermal diffusion phenomenon such as a solid state reaction and a solid-liquid state reaction.

Since such heat treatment is necessary, it is impossible to apply ceramics directly to a substrate having a low-heat resistance such as a plastic substrate, and also it is necessary to prepare a sintering furnace which makes the manufacturing process complicated. Such heat treatment may also change the microscopic size characteristics or physical properties of a film or microstructure.

A method of forming a film or a microstructure without any heat treatment, which film or microstructure has high density and strength and is made of brittle ultrafine particles bonded at a desired bonding strength, has long been desired.

SUMMARY OF THE INVENTION

The invention has been made under such circumstances and aims at providing a method of forming a film or a microstructure without any heat treatment, which film or microstructure has high density and strength and other desired characteristics and is made of brittle ultrafine particles bonded at a desired bonding strength.

In order to achieve the above object, the invention provides a method of forming a brittle ultrafine particle shaped body at a low temperature, wherein a mechanical impact force is applied to the brittle ultrafine particles supplied to a substrate in order to break the particles and bond them together.

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BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic diagram showing a structure of an ultrafine particle film forming system.

Fig. 2 is a schematic diagram showing a structure of another ultrafine particle film forming system.

Fig. 3 is a schematic diagram showing a structure of yet another ultrafine particle film forming system.

Fig. 4 is a TEM image showing a cross section of an interface between a film formed at room temperature and a silicon substrate.

Fig. 5 is a TEM image showing a cross section of particles used as a source material and its electron beam diffraction image.

Fig. 6 is a TEM image showing a plan view of a film formed at room temperature and its electron beam diffraction image.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Embodiments of the invention will be described in detail with reference to the accompanying drawings.

Referring to Fig. 1, in a chamber 2 of an ultrafine particle film-forming system 1a, a substrate 3 and an ultrafine particle supply apparatus 4 are mounted. In this embodiment, a nozzle is used as the ultrafine particle supply apparatus 4. A film is to be formed on this substrate 3. If necessary, a mechanical impact force loading apparatus 5 is disposed along a motion direction of the substrate 3.

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The nozzle 4 is used for applying brittle ultrafine particles to the substrate 3 to form an ultrafine particle deposit 11 or an ultrafine particle pressed body 16. The ultrafine particle deposit 11 is a deposit of ultrafine particles on the substrate 3 supplied from the nozzle 4, and not bonded to each other. The ultrafine particle pressed body 16 is a body of ultrafine particles blown from the nozzle 4 and bonded together by a mechanical impact force caused by the blowing force of the nozzle 4. The substrate 3 is mounted on a substrate driver apparatus 6 so that it can be moved in the chamber 2 along a horizontal plane. The nozzle 4 may be made moveable in the chamber 2 relative to the substrate 3.

The mechanical impact force loading apparatus 5 is used for applying a mechanical impact force to the ultrafine particle deposit 11 on the substrate to break the brittle ultrafine particles 7 and form an ultrafine particle film 12.

Next, the operation of forming a film will be described. Ultrafine particles 7 are mixed with a carrier gas in the nozzle 4 and blown onto the substrate 3 while the substrate 3 is moved relative to the nozzle 4 to form the ultrafine particle deposit 11. Alternatively, ultrafine particles 7 are forced to collide with the substrate to break and bond to each other to form the ultrafine particle pressed body 16. If this ultrafine particle pressed body 16 has physical properties sufficient for the target ultrafine particle film 12, this pressed body 16 may be used as the final ultrafine particle film 12 and the film forming process may be terminated. If necessary, a mechanical impact force may be applied to the ultrafine particle pressed body 16 formed on the substrate to further break the ultrafine particles of the pressed body 16 to form an

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ultrafine particle film 12 having a greater bonding strength. An ultrafine particle film will not be formed unless a mechanical impact force is applied to the ultrafine particle deposit 11.

5 The mechanical impact force to be applied to the ultrafine particle deposit 11 or ultrafine particle pressed body 16 in order to break ultrafine particles, may be realized by: accelerating brittle ultrafine particles by applying an electrostatic field or by using a gas carrier to
10 blow them onto a substrate; by using a high rigidity brush or roller rotating at high speed, pressure needles moving up and down, or a piston moving at a high speed utilizing an explosion compression force; or by using ultrasonic waves. In this case, the carrier gas may be dry air without using a
15 specific gas such as an inert gas.

 It is necessary for the ultrafine particles to be broken easily by the mechanical impact force generated either by the blowing force of the nozzle 4 or by the mechanical impact force loading apparatus 5. To this end,
20 it is essential that the generated mechanical impact force is dominant over a brittle fracture strength of the ultrafine particles.

 In order to satisfy this condition, raw materials of ultrafine particles may be pre-processed: to adjust by
25 changing the pre-sintering temperature of the brittle ultrafine particles; to form secondary cohesive particles of about several hundred nanometers in diameter by heating the brittle ultrafine particles of several ten nanometers or smaller in diameter which are formed by chemical methods
30 such as alkoxide colloid pyrolysis, or by physical method such as using vapor deposition and sputtering; or to form particles with cracks by processing them for a long time in

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a mill such as a ball mill, a jet mill, a bead mill or a vibration mill. By applying a mechanical impact force to such raw materials of the ultrafine particles, they can be broken down to have a diameter of 100 nm or smaller so that a clean new surface can be formed and low-temperature bonding becomes possible. In this manner, brittle ultrafine particles can be bonded at room temperature and a film having high density and strength can be formed. According to experiments performed by the inventor, it is considered that such breakage of ultrafine particles by the mechanical impact force is not likely to occur if the diameter of each brittle ultrafine particle of raw material is 50 nm or smaller. If the mechanical impact force is generated by the blowing force of the nozzle, this mechanical impact force is not sufficient for impact breakage if the particle diameter is too large. It is therefore preferable that the particle diameter is set in the range of from about 50 nm to 5 μ m for each of the above-described methods of applying the mechanical impact force.

When films were formed by using brittle ultrafine particles of lead zirconate titanate oxide (PZT) or titanium dioxide (TiO_2) prepared in the above manner, dense films having a density that is 95% or more of the theoretical density were able to be formed, and the adhesion force to a silicon or stainless substrate was 50 MPa or higher.

A process of forming a brittle ultrafine particle film will be described by using as an example a process of colliding brittle ultrafine particles mixed with a carrier gas with a substrate to break the particles. The ultrafine particles which collide with the substrate first, anchor to the substrate (anchoring effect) to form an underlying layer. In this case, the ultrafine particles may be partially bonded depending upon the combination of the

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materials of the particles and the substrate. However, this partial bonding is not necessarily required but it is sufficient if the underlying layer has such an adhesion force that the layer is not peeled off while brittle
5 ultrafine particles collide with it thereafter. Ultrafine particles colliding with the underlying layer break apart, along with those particles on the surface of the underlying layer. Those broken particles are bonded together at a low temperature to form a strong deposit. In this manner, while
10 the collided brittle ultrafine particles are being deposited over the substrate, breakage and bonding occur simultaneously. The thickness of a film of brittle ultrafine particles to be formed on the substrate is determined based upon whether or not the breakage impact
15 force can be maintained effectively.

The method of applying the mechanical impact force includes, in addition to the method of blowing brittle ultrafine particles from a nozzle toward a substrate, a method of using a brush or roller rotating at high speed, or
20 using pressure needles. In thinly depositing (developing) brittle ultrafine particles on a substrate, they may be pushed against the substrate by using the roller to press them without breakage, without necessarily using the nozzle. In some case, they may be only gently dropped down and
25 deposited.

As a method of mechanically breaking brittle ultrafine particles, high intensity ultrasonic waves may be applied in a contact or non-contact manner. In this case, ultrasonic waves strong enough to break the particles are
30 applied to the brittle ultrafine particles that are either thinly deposited on or mechanically pressed against a substrate, in order to break the particles by the impact force induced by the ultrasonic waves. Although ultrasonic

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waves can be applied in a contact or non-contact manner, sound energy can be transmitted more efficiently if the ultrasound source is made in direct contact with the pressed body or via an impedance matching medium. The ultrasonic wave may be spatially converged by using an ultrasonic lens to focus it to one point, thereby breaking ultrafine particles at this point. In this method, only a particular point of the particle pressed body may be bonded at a low temperature. If an ultrasonic wave is directly applied to a press mold or roller for molding a particle pressed body, the mechanical impact force by ultrasonic waves can be generated by a simple process.

An ultrafine particle film forming system 1b according to another embodiment shown in Fig. 2 has an ultrafine particle supply adjusting blade 17 and a mechanical impact force loading apparatus 5.

The ultrafine particle supply adjusting blade 17 adjusts the supply amount of brittle ultrafine particles 7 to a substrate 3 by scraping and planarizing the surface of an ultrafine particle deposit 11 or an ultrafine particle pressed body 16. The supply amount is controlled by adjusting the height of the blade 17.

The mechanical impact force loading apparatus 5 has, as shown in Fig. 2, an impact force loading roller 13 and a high intensity ultrasonic wave applying apparatus 14.

The impact force loading roller 13 is used for forming an ultrafine particle film 12 by directly applying a mechanical impact force to the supply amount adjusted ultrafine particle deposit 11 on the substrate 3. The high intensity ultrasonic wave applying apparatus 14 drives the impact force loading roller 13. The impact force loading roller 13 may be any other body so long as it can load the

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mechanical impact force to the ultrafine particle deposit 11 or ultrafine particle pressed body 16. For example, in an ultrafine particle film forming apparatus of another embodiment shown in Fig. 3, a number of impact force loading 5 needles 15 are used. The embodiment of the invention described above may be applied not only to forming a dense film but also to a porous film, by adjusting raw material particles and film forming conditions such as a film forming speed. A porous film is effective for applications 10 requiring a large specific surface area, such as electrodes of a fuel battery and a super capacitor.

(Experimental Examples)

(1) Introduction

For application of piezoelectric material to a 15 micro actuator or the like, it is important to form a thick film of about 20 μm and then finely pattern it. Lead zirconate titanate oxide (PZT) of about 0.1 μm in diameter, typical piezoelectric material, was mixed with a gas to make it aerosol and blow it via a nozzle to a substrate in the 20 form of a high speed jet flow to form a film. This method is more advantageous in that a dense thick film can be formed in a dry process without a binder and fine patterns can be formed easily, as compared to a screen printing method. Unlike general film-forming techniques, it can be 25 considered that the electrical characteristics of a film formed by this method are greatly influenced by the heat treatment conditions and the structure change in ultrafine particles such as PZT particles caused when they collide with a substrate. The microscopic structure of films was 30 investigated in order to clarify the film forming mechanism and improve the film characteristics.

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(2) Experimental Method

PZT ultrafine particles were ejected from a nozzle having an opening size of 5 mm x 0.3 mm and deposited on a substrate by using an aerosol gas deposition method. The substrate used included a silicon substrate, a SUS 304 substrate, and a Pt/Ti/SiO₂/Si substrate. The PZT particles had a composition of Zr/Ti : 52/48, a specific surface area of 2.8 m²/g, and an average particle diameter of 0.3 μm, and were heated and dried at a low pressure of 10⁻² Torr. The carrier gas was helium and dried high purity air, and the particle speed was controlled by the carrier gas flow rate. The microscopic structure of a PZT film having a thickness of 20 μm formed in the above manner was observed as TEM images and electron beam diffraction images.

15 (3) Results and Conclusions

Fig. 4 is a TEM image showing the cross section of a film formed on an Si substrate at room temperature. There is a damage layer of about 0.15 μm at an interface between the Si substrate and a PZT layer, the damage layer being formed through collision of PZT ultrafine particles with the substrate. It can therefore be presumed that a mechanical impact force was generated by the collision of PZT ultrafine particles, the impact force exceeding the plastic flow pressure (Vickers hardness: 5 to 12 GPa) of Si. Since the brittle fracture strength of PZT ultrafine particles is 2.3 to 4 GPa, it can be expected that such a large mechanical impact force sufficiently broke PZT ultrafine particles and generated a new surface.

According to the composition analysis through EDX, thermal diffusion into the Si substrate was hardly recognized. Voids were hardly found in the film and at the

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interface, indicating that the dense film was formed at room temperature.

Fig. 5 is a TEM image in cross section of raw material particles, and Fig. 6 is a TEM image in plan view of a film deposited at room temperature on a Pt/Ti/SiO₂/Si substrate. Raw material particles were partially cohesive and had inner strain and defects. Particles were almost single crystals as determined from an electron beam diffraction image when considering the particle diameter near that observed by SEM. The crystal grain size was concentrated in a range of about 0.1 to 0.5 μm . In contrast, an as-deposited film at the room temperature had a polycrystalline structure that there was no significant change in the composition of the film both in the cross sectional direction and in-plane direction, with large crystal particles of about 0.1 to 0.2 μm approximately of the original size being embedded and surrounded with small crystal particles of about 10 to 40 nm, and also that a number of fine contrasts were observed which might be generated by strain. From these studies, it can be understood that some of PZT ultrafine particles are broken finely and form fine crystals of about several ten microns because of collision with the substrate during the film forming process.

As described above, according to the present invention, a mechanical strength (brittle fracture strength) of brittle ultrafine particles is adjusted in accordance with a mechanical impact force to be applied to the brittle ultrafine particles so that the impact breakage occurs, or the mechanical impact force is applied in accordance with the mechanical strength of the brittle ultrafine particles.

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In this manner, a clean new surface is formed and the brittle ultrafine particles are bonded together so that an ultrafine particle film having high density and high strength can be formed at room temperature. The new surface
5 formed through breakage of the brittle ultrafine particles is again bonded in a very short time on site by the pressure applied to the brittle ultrafine particles. Since the time taken to bond the particles again is very short, the film forming atmosphere may be the atmospheric air without using
10 a specific atmosphere such as an inert gas atmosphere. As the size of the brittle ultrafine particles becomes about several ten nanometers, the surface energy increases to enhance bonding, and generation of voids can be prevented which are otherwise formed because of undefined shapes of
15 particles. A dense film or microstructure in the order of several tens nanometers in diameter can be obtained.

Since brittle material such as ceramics having a high melting point can be formed on a substrate at room temperature, the surface of a substrate made of a material
20 having a low melting point such as plastics can be coated with ceramics. A vinyl film was attached to a stainless steel substrate, and brittle ultrafine particles of PZT were blown to the surface of the vinyl film. It was possible to form at room temperature a very rigid shaped body having a
25 density of 97% and an adhesion force of at least 15 MPa. It was able to form a ceramic material having a nanometer size crystal structure finer than its raw material ultrafine particles, through breakage impact. The density of the shaped body was higher than 95% of the theoretical density.
30 Therefore, the temperature of heat treatment for grain growth was able to be lowered. For example, in the case of lead zirconate titanate (PZT), the temperature was able to be lowered by about 300°C as compared to a usual sintering

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temperature. A lowered grain growth temperature was thus confirmed.

As the brittle ultrafine particles broken into still finer particles having a size under 80 nanometer have 5 many fine new surfaces, the surface energy of the brittle ultrafine particles without heating increases to enhance bonding of them.

Therefore it is required that at least a part of brittle ultrafine particles supplied to a substrate to be 10 broken into finer particles having a diameter of 80 nanometer or less by applied mechanical impact force in the process of the present invention.

Further, by not applying heat to the shaped ceramic body, such as ceramic film having polycrystal 15 structure with nanometer order crystallite size formed by the process of the present invention, the fine crystallites in the body do not grow and are kept in fine broken size; this brings improved elasticity and strength of the body, along with improved characteristics toughness.

As apparent from the above description of the 20 invention, brittle ultrafine particles such as ceramics are broken into particles of about several ten nanometers by applying a mechanical impact force. A clean new surface can be formed on site, and by utilizing this surface, ultrafine 25 particles are bonded together. In this manner, a shaped body such as a film and a microstructure of high density and high strength can be formed without heating.

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CLAIMS:

1. A method of forming a shaped body of brittle ultrafine particles without heating, which method comprises:

5 applying a mechanical impact force to raw brittle ultrafine particles supplied onto a surface of a substrate,

(i) to break the raw brittle ultrafine particles, thereby forming broken brittle ultrafine particles finer than the raw brittle ultrafine particles and having clean new surfaces and immediately thereafter bond together the
10 clean new surfaces of the broken brittle ultrafine particles without heating, or

(ii) to break the brittle ultrafine particles, thereby forming broken brittle ultrafine particles finer than the raw brittle ultrafine particles and having clean
15 new surfaces and immediately thereafter bond the clean new surfaces of the broken brittle ultrafine particles together as well as to the substrate without heating, thereby forming the shaped body of the brittle ultrafine particles on the surface of the substrate, wherein:

20 the raw brittle ultrafine particles have a particle diameter of 50 nm to 5 μ m and a brittle fracture strength weaker than the applied mechanical impact force;

the broken brittle ultrafine particles have a diameter of 100 nm or less; and

25 the formed shaped body of the brittle ultrafine particles has a density that is 95% or more of its theoretical density.

2. The method according to claim 1, wherein the mechanical impact force is applied by:

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high-speed collision of the brittle ultrafine particles with the substrate by application of an electrostatic field or use of a jet of a carrier gas;

5 pressing the brittle fine particles by using a rotating high rigidity brush or roller, pressure needles moving up and down, or a piston moving by utilizing an explosion compression force; or

ultrasonic waves.

3. The method according to claim 1 or 2, wherein the
10 brittle ultrafine particles have been pre-processed so that the mechanical impact force becomes dominant over a brittle fracture strength of the ultrafine particles.

4. The method according to claim 3, wherein the pre-processing is conducted by:

15 adjusting a pre-sintering temperature of the brittle ultrafine particles;

formation of secondary cohesive particles of from 50 μm to 5 μm in diameter by heating the brittle ultrafine particles; or

20 formation of cracks in the brittle ultrafine particles by processing the particles by the use of a milling method selected from the group consisting of a ball mill, a jet mill, a bead mill and a vibration mill.

5. The method according to any one of claims 1 to 4,
25 wherein the applied mechanical impact force breaks down a portion of the ultrafine particles supplied to the substrate into particles with a diameter of 80 nm or less.

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6. A method of forming a film of brittle ultrafine particles of a ceramic material onto a surface of a substrate, at least the surface of the substrate being made of a material selected from the group consisting of plastic,
5 silicon, stainless steel and Pt/Ti/SiO₂/Si, which method comprises:

applying a mechanical impact force to raw brittle ultrafine particles supplied onto the surface of the substrate to break the raw brittle ultrafine particles,
10 forming smaller particles having clean and active new surfaces and to immediately thereafter bond the clean new surfaces of the smaller particles together as well as to the substrate, without heating, thereby forming the film,

wherein the raw brittle ultrafine particles have a
15 diameter of 50 nm to 5 μ m and a brittle fracture strength lower than the mechanical impact force and a plastic flow pressure of the material of the substrate surface;

wherein the smaller particles formed by breaking the raw brittle ultrafine particles have a diameter of
20 100 nm or less;

wherein the mechanical impact force is applied by at least one of:

(i) blowing the raw brittle ultrafine particles with a carrier gas onto the substrate surface;

25 (ii) pressing the raw brittle ultrafine particles onto the substrate surface by a rotating rigid brush or roller, pressure needles moving up and down or a piston moving by an explosion compression force; and

(iii) ultrasonic waves; and

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wherein the formed film of the brittle ultrafine particles has a density that is at least 95% of a theoretical density of the ceramic material.

7. The method according to claim 6, wherein the
5 ceramic material is a member selected from the group consisting of lead zirconate titanate oxide (PZT) and titanium dioxide.

8. The method according to claim 6, wherein the ceramic material is lead zirconate titanate oxide (PZT).

10 9. The method according to any one of claims 6 to 8, wherein the raw brittle ultrafine particles have been pre-processed so that they have a brittle fracture strength lower than the applied mechanical impact force, the pre-processing being conducted by:

15 (a) changing a pre-sintering temperature of the brittle ultrafine particles to adjust the brittle fracture strength;

(b) forming secondary cohesive particles of the brittle ultrafine particles which are formed by a chemical
20 or physical method; or

(c) forming cracks in the brittle ultrafine particles by processing the particles in a mill.

10. The method according to any one of claims 6 to 9, wherein the mechanical impact force is applied to the raw
25 brittle ultrafine particles by blowing the brittle ultrafine particles with a carrier gas against the substrate surface.

11. The method according to any one of claims 6 to 9, wherein the mechanical impact force is applied to the raw brittle ultrafine particles by pressing the brittle

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ultrafine particles laid on the substrate against the substrate by a rotating rigid brush or roller, by pressure needles moving up and down or by a piston moving by an explosion compression force.

5 12. The method according to any one of claims 6 to 9, wherein the mechanical impact force is applied to the raw brittle ultrafine particles by ultrasonic waves.

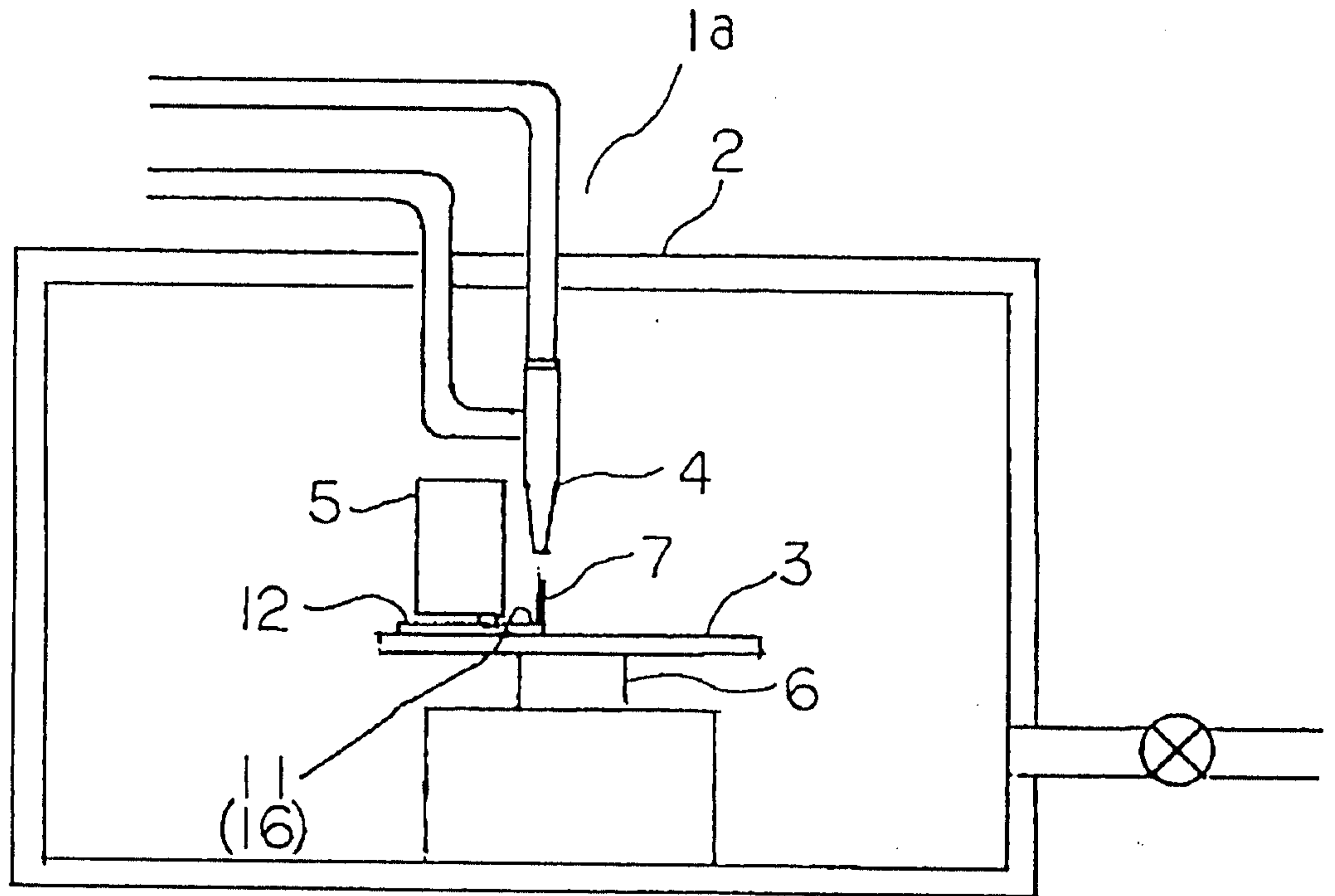
13. The method according to any one of claims 6 to 12, wherein the applied mechanical impact force is enough to
10 break the raw brittle ultrafine particles into still finer particles, at least a part thereof having a diameter of 80 nm or less.

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FIG. 1



F I G . 2

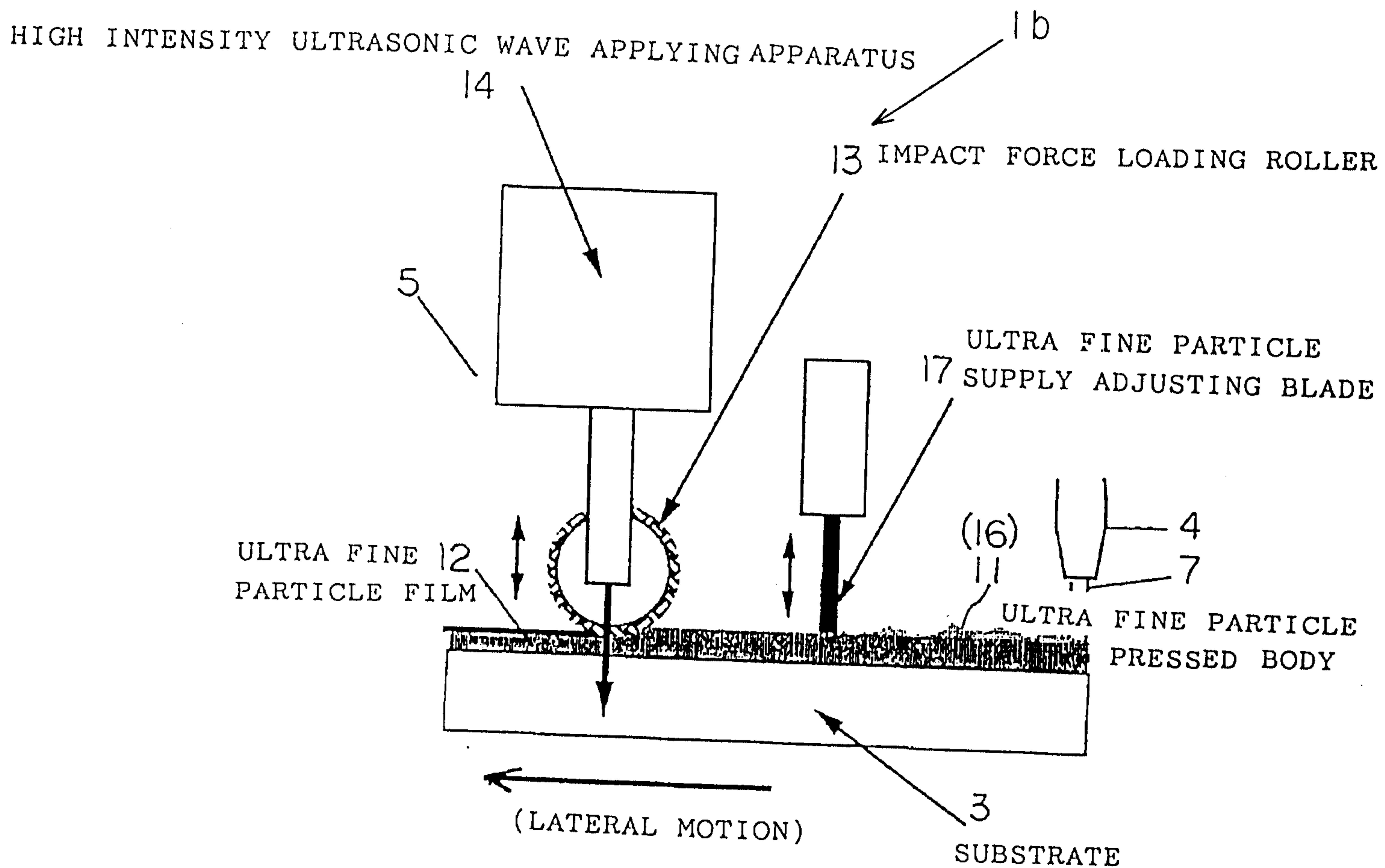


FIG. 3

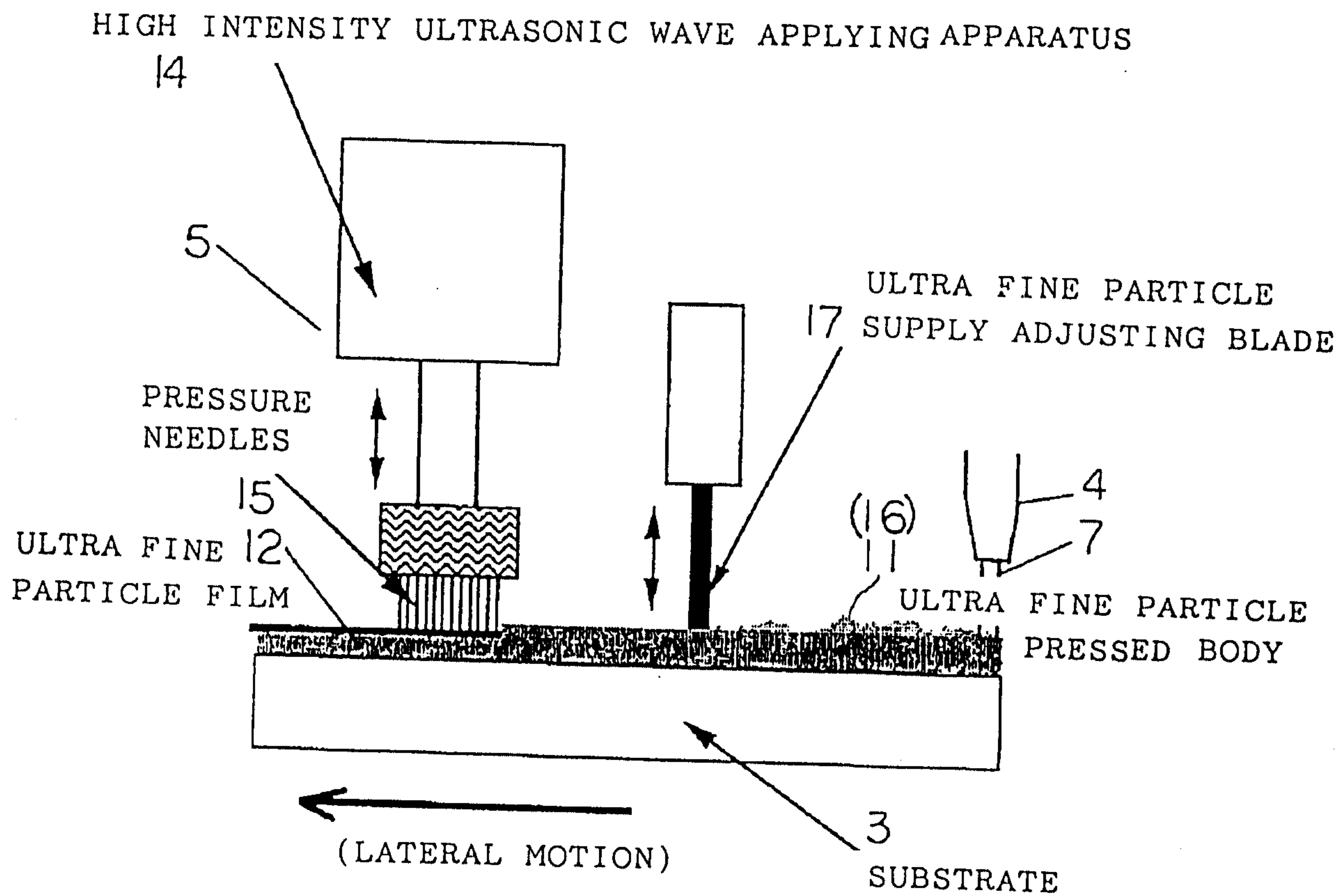
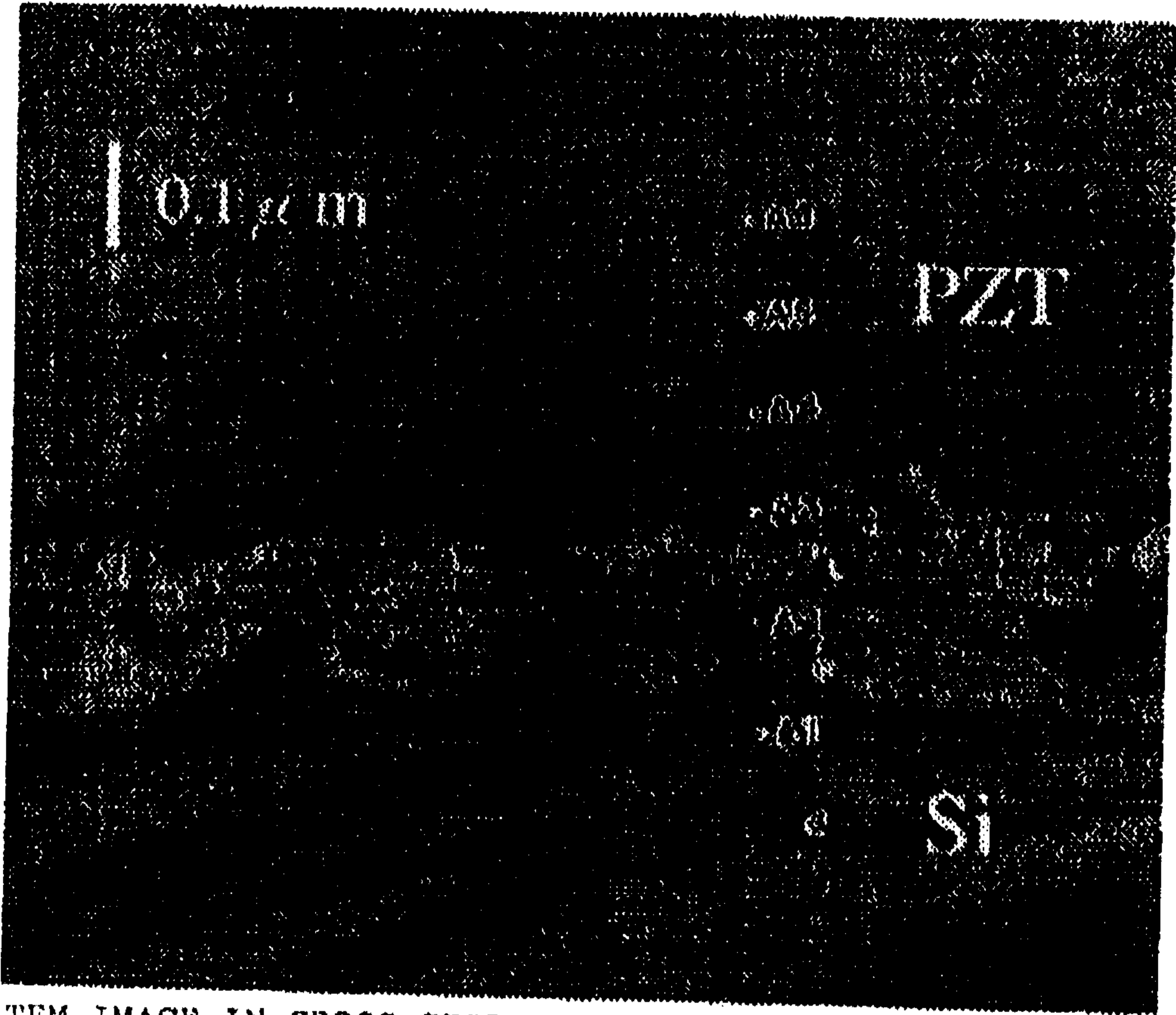
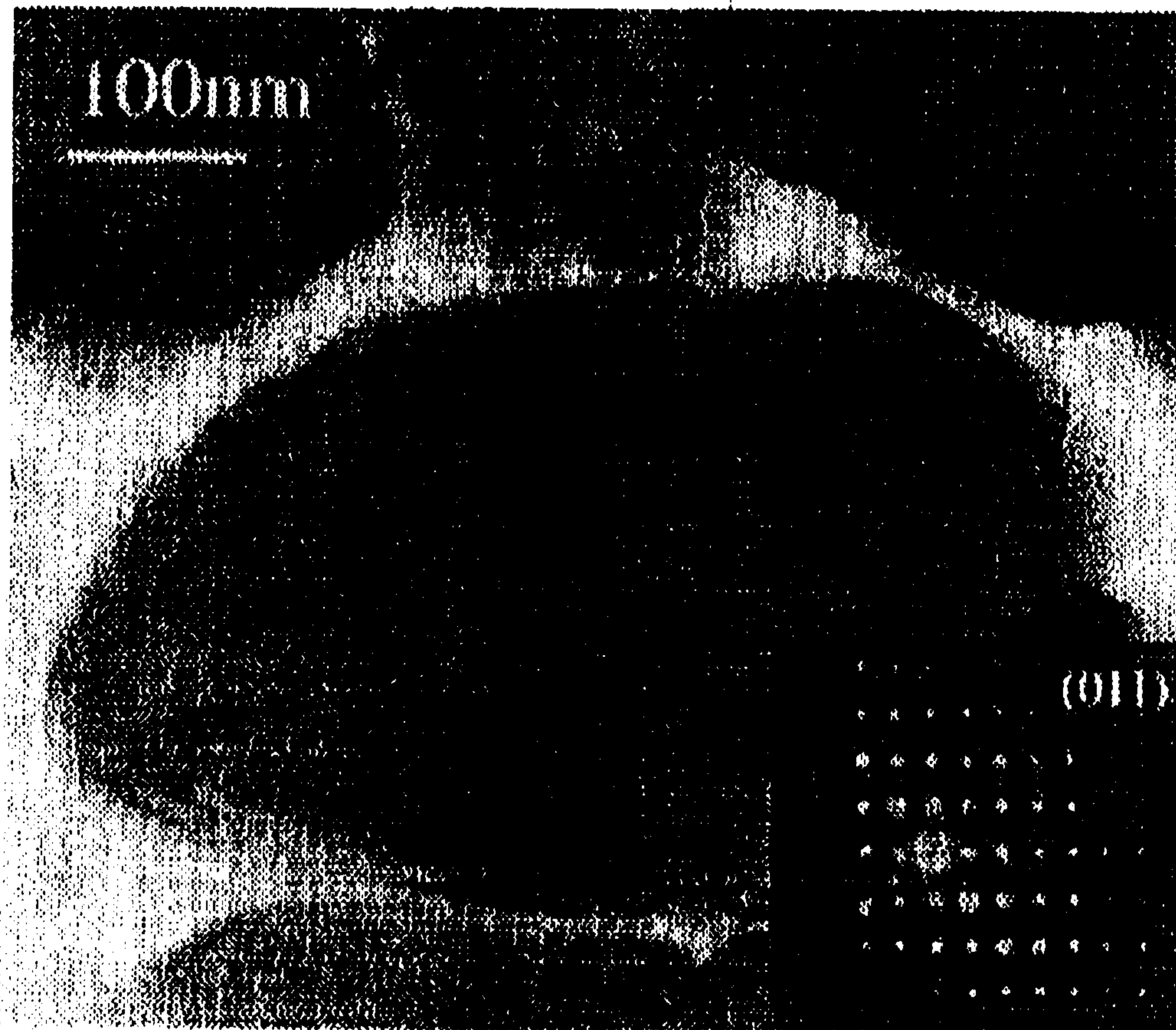


FIG. 4



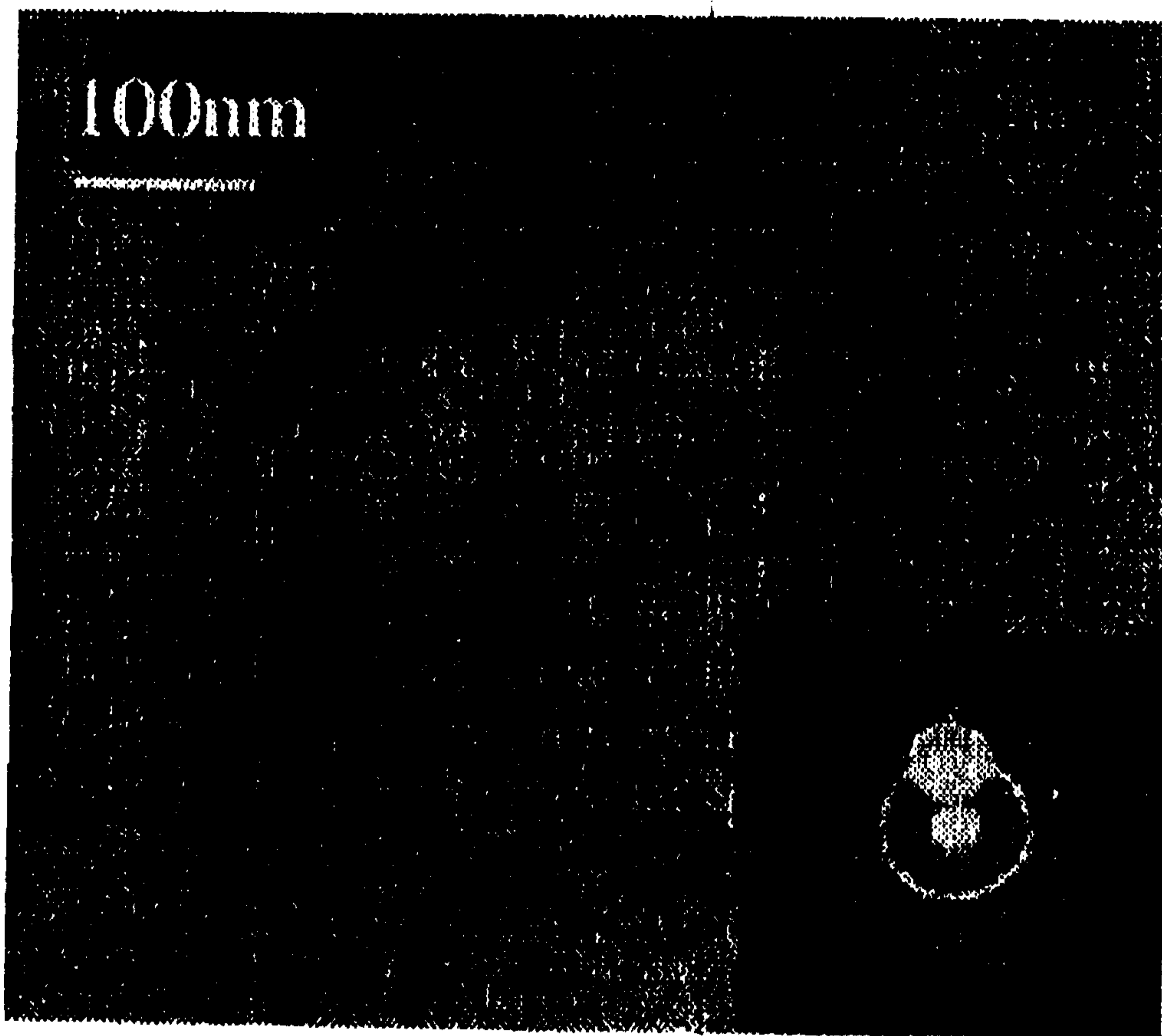
TEM IMAGE IN CROSS SECTION OF INTERFACE BETWEEN ROOM TEMPERATURE DEPOSITED FILM AND SILICON SUBSTRATE

FIG. 5



TEM IMAGE IN CROSS SECTION OF RAW MATERIAL PARTICLES

F I G . 6



TEM IMAGE OF ROOM TEMPERATURE DEPOSITED FILM AND
DIFFRACTION IMAGE

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