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Determination of cubic boron nitride synthesized by ion implantation

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Synthesis of cubic boron nitride in equilibrium condition requires very high severe condition. In this paper, we report the experiment to make cubic boron nitride by nitrogen ion implantation to boron film. The velocity of ion beam accelerated by electrical potential is one hundred times higher than that of explosive power of chemical reaction, such as dynamite, which means the temperature of the implanted ion is as high as 500 million degrees. On the experiment, boron film was prepared on a single-crystal silicon substrate by RF sputtering. It was implanted by N_2^+ ion with ion accelerating voltage 30kV, at doses of $1.0\text{x}10^{17}$ ions/cm^2, etc. The microstructure identification was carried out by transmission electron microscopy. The t-BN, c-BN and w-BN were confirmed to be synthesized in the film.

Key words: boron nitride, ion implantation, microstructure, TED

1. INTRODUCTION

Recently, the age of non-equilibrium has come. Although Non-equilibrium materials, such as amorphous, alloy semiconductor, duralumin and composite materials are usually unstable thermodynamically under earth environment, they are stable as long as they stand for long use. Since the ion implantation method makes extreme severe condition dynamically, it is the unique method to study particle-dynamics on the surface materials. The velocity of ion beam accelerated by electrical potential is one hundred times higher than that of explosive power of chemical reaction, such as dynamite, which means the temperature of the implanted ion is as high as 500 million degrees. Using this extreme energy, we investigate the microstructure of boron nitride films synthesized by ion implantation.

Although there are many molecular dynamics simulations of particle reaction on surface, few experimental proofs are shown for the degree of pressure and temperature when the ion makes an attack on the materials surface.

2. ESTIMATE PRESSURE THAT OCCURS BY THE COLLISION OF IONS

The evaluation of dynamical pressure, which occurs by the collision of ions, is much difficult. The ionized particles have to handle by quantum mechanics in consideration of the waviness of the particle. As the first approximation this time we tried to think by Newtonian mechanics. On the kinetic theory of gases, the pressure from gas particles is same as the impulse from the collision that happens on the unit time and unit area.

For example, the nitrogen molecule accelerated by 50kV electric potential (as V_0) attacks the surface with 10μA/cm^2 (I_0=10μA/cm^2 =$1.0\text{x}10^{-1}$Csec^{-1}m^{-2}). The mass of a nitrogen molecule m and the unit charge of electron e are

$$m = 4.6\times10^{-26}(\text{kg}),\quad e = 1.6\times10^{-19}(\text{c}). \quad (1)$$

The energy of a nitrogen molecule E is

$$E = eV_0 = 8.0\times10^{-15}(\text{J}). \quad (2)$$

The velocity of a nitrogen molecule v is

$$v = \sqrt{2E/m} = 5.9\times10^{5}(\text{msec}^{-1}). \quad (3)$$

The number of particles colliding per one-second n is

$$n = I_0 / e = 6.3\times10^{17}(\text{sec}^{-1}\,\text{m}^{-2}). \quad (4)$$

The pressure P that occurs is

$$P = 2mvn = 3.4\times10^{-2}(\text{Pa}). \quad (5)$$

The high pressure cannot occur by the static handling. In other words, the static power that the flow of the ion gives to injection surface is extremely small because the electric flow quantity is very small.

Therefore we are trying to handle dynamically the force that occurs by the collision of a particle. The nitrogen molecule collides in the same condition to an aluminum film of 1μm thickness. It is accelerated by 50kV and collides to a film in the speed of 590kmsec^{-1}. On this time all the kinetic energy is changed for elastic energy. Assume all the kinetic energy of the particle is converted to the elastic energy on this column part compressed by the collision. The module of elasticity C is the ratio of compression per unit of area and length, therefore the spring constant k of this dynamical part is

$$k=C\cdot S/L, \tag{6}$$

where the attacked area is S, thickness of film is L.

This column part have been compressed with length x and all the kinetic energy of the particle is converted to the elastic energy E.

$$E=\frac{1}{2}kx^2, x=\sqrt{2E/k} \tag{7}$$

The force F that occurs is

$$F=kx=\sqrt{2Ek}. \tag{8}$$

The pressure P that occurs is

$$P=F/S=\sqrt{\frac{2EC}{Ls}}. \tag{9}$$

Assume C is 100GPa, L is 10^{-6}m, and S is approximately 10^{-19}m^2 (as the radius of the nitrogen atom is 0.17nm.), we estimate the pressure

$$P=4\times10^{12}(\text{Pa}) . \tag{10}$$

The outbreak pressure becomes 40 million atmospheres.

In fact there is energy scattering on real ion implantation. Also, the area of taking a collision force is wider than this, it seems that the pressure is not such high, but it will be high enough pressure composed such as diamond.

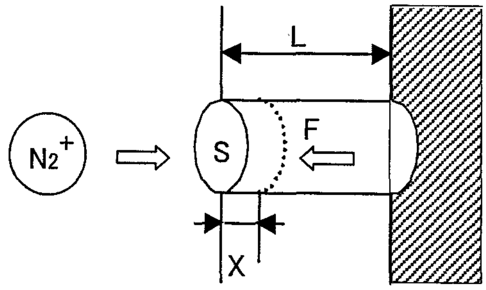

Fig.1 Dynamic effect when a nitrogen molecule attacks the film. It is assumed all the kinetic energy is changed to the elastic energy and it makes high pressure.

3. EXPERIMENTAL PROCDURES

To determine boron nitride from unirradiated film, we prepared boron films by 13.56MHz radio frequency (RF) sputtering on a silicon single crystal substrate which dimension is (1,0,0). A boron target, which is 2-inch diameter, 99.5% purity, was set in the sputtering chamber, and silicon substrate was put against from boron target with the distance of 40mm. The gas pressure was 6.5Pa. A presputtering with 30 minutes was carried out to remove the initial oxide from the target. The substrate temperature measured 300 degrees during process by thermocouple put at the back surface of substrate.

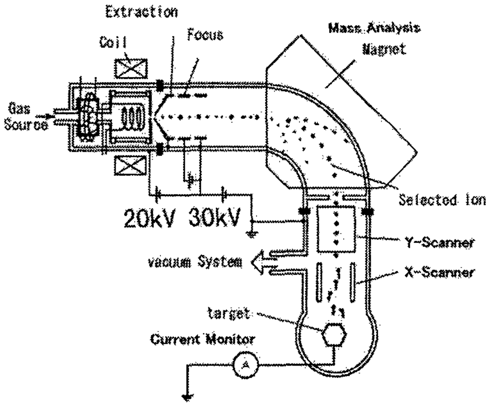

Fig.2 Ion implantation equipment

Figure 2 shows the ion implantation equipment. Nitrogen Gas was used to generate charged ions in a hollow-cathode-type ion source. The ions were extracted from the ion source by bias voltage 10kV or 20kV, and then accelerated up to 30kV. The accelerated ions pass through the magnetic filed where the mass of ions were selected. In this experiment, only diatomic, single nitrogen ions N_2^+ were selected. They are accelerated totally up to 50 kV, scanned like an electron beam of an oscilloscope by electric fields in horizontal and vertical directions by which ions can irradiate materials with any pattern. Boron film was implanted at doses from $1\times10^{17}\text{ions/cm}^2$ to $4\times10^{18}\text{ions/cm}^2$. The irradiated

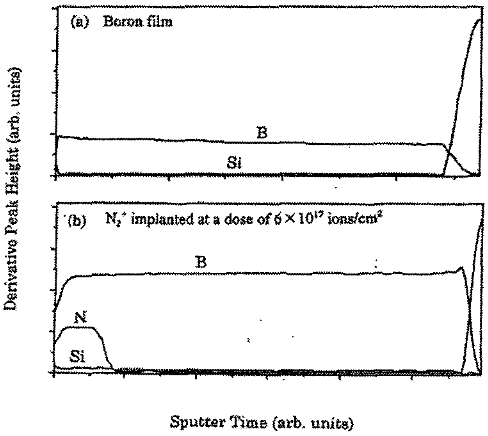

Fig.3 AES depth concentration profiles:(a) before implantation and (b) after implantation at the dose 6×10^{17} ions/cm²

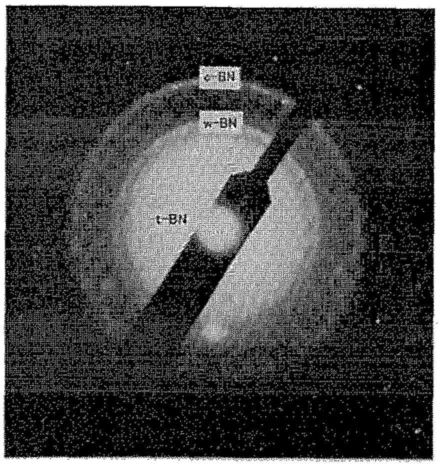

Fig.4 TED pattern of BN film implanted at the dose of $4x10^{17}$ inos/cm^2

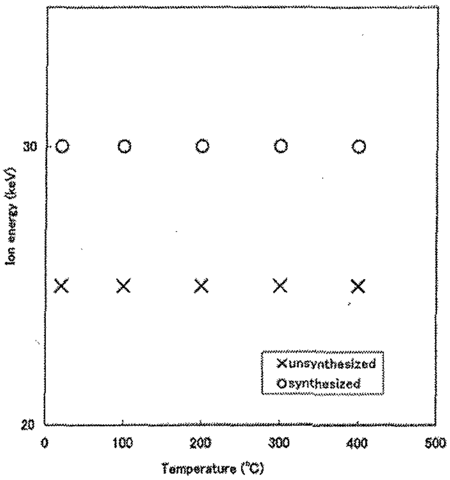

Fig. 6 c-BN and w-BN synthesis conditions

area was chosen so as to keep the ion beam flux constant at 10μA/cm^2. A thermocouple was set at the back surface of substrate to measure the temperature during irradiation process. The temperature increase is up to 20 degrees above the room temperature.

To confirm the formation of boron-nitride in the implanted film, Auger electron spectroscopy (AES) was employed for the chemical composition analysis of as-sputtered boron films and ion-implanted films. Also, the micro-structural identification of implanted films was carried out by transmission electron microscope (TEM) and transmission electron diffraction (TED) method by a JEOL H-9000 microscope.

4. RESULTS AND DISCUSSIONS

Before implantation, as-sputtered born film was observed by an Atomic Force Microscope (AFM), TEM and TED to analyzed surface structure. It was observed only some type of nano-order cluster by AFM. By TED observation, the diffraction pattern showed two halo-like rings corresponding to rhombohedral boron (1,0,0) and (2,1,1). It shows that the film is in amorphous state.

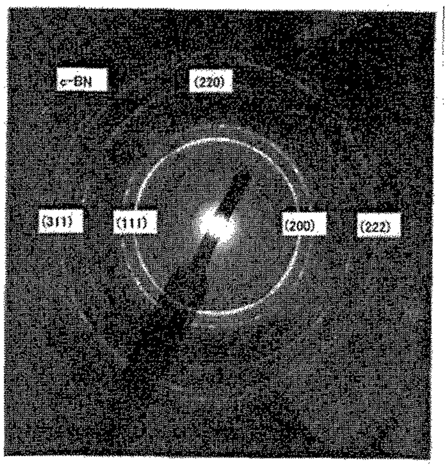

Fig.5 TED Pattern of BN film implanted at the dose of $2x10^{18}$ inos/cm^2

The formation of boron nitride after implantation was confirmed by AES chemical composition analysis. Figure 3 shows the Auger depth profiles on as-sputtered boron film and nitrogen-implanted film. Compared with the as-sputtered film profile, the profile of the implanted film shows that nitrogen atoms were embedded in the born film estimated 0.2-0.3μm depth. Compared with as-sputtered film TED pattern, it was cleared to have obtained boron nitride by diffraction pattern. Figure 4 shows TED pattern at the dose of $1x10^{17}$ ions/cm^2. A t-BN halo rings exists and crystallinestate was not observed at this dose. At the dose of $4x10^{17}$ions/cm^2 the crystallization began to be observed. It was indicated that the implanted nitrogen atoms are combined with boron atoms. Figure 5 shows two rings corresponding to w-BN and c-BN. In the highest dose-implanted film, that is $2x10^{18}$ions/cm^2, the diffraction pattern figure 5 clearly shows crystallinestate of c-BN.

In these experiments t-BN was found to appear first at the early stage of low dose implantation. t-BN is similar to the structure of hexagonal boron nitride (h-BN) but is highly structurally disordered in the c direction. The difference between h-BN and t-BN is the distance for c direction of two planes. h-BN is 0.333nm, and t-BN is 0.356nm. By the TED method, these can be determined easily.

The similar experiment was carried out at the lower ion implantation energy of 25 kV. At the 25 kV ion energy implantation, c-BN formation was not found. Figure 6 shows the formation results vs. substrate temperature. This proves that the ion

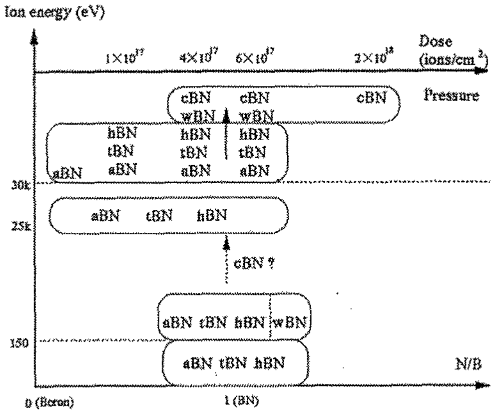

Fig. 7 Phase formation of BN under ion bombardment

energy has a critical point to make high pressure.

5. CONCLUSIONS

Boron nitride films were synthesized by the nitrogen ion implantation of boron films. After implantation a mixture of t-BN, c-BN and w-BN phases exists in the films. The phases of c-BN and w-BN, that is the high-pressure phases, appeared with an increase of implantation dose.

Figure 7 reviews the all process. It shows that many phases appear under ion implantation. The low-density phase t-BN appeared first at the low dose implantation. The increase of implantation dose cause the internal stress in the film, which causes the crystal growth and make high-pressure phase c-BN. At the last stage all phases change to c-BN phase finally.

6. ACKNOWLEDGMENTS

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