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Reaction between Si Substrates and High-Density, High-Temperature Zr Plasma Produced by Ion-Beam Evaporation

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Zirconium thin films have been deposited at room temperature on single crystal Si substrates by an intense pulsed light ion-beam evaporation (IBE) method. The microstructures of the prepared thin films were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). In some thin films, peaks for not only Zr but also $ZrSi_2$ phases appeared in the XRD patterns. Furthermore, polycrystalline Si grains were also detected. Cross-sectional back-scattered SEM images of the prepared thin films showed that the thin films containing the polycrystalline Si grains had thickness of approximately 1μm. The interface between the thin films and the substrates were undulated. From these results, portions of substrates in the vicinity of the surface were considered to be melted by the heat of high-density and high temperature Zr ablation plasma. A part of the melt was mixed and reacted with Zr to form $ZrSi_2$ grains in the thin films. The rest was solidified to form polycrystalline Si grains. In this research, we successfully developed a novel thin film preparation method in which ablation plasma species were simultaneously deposited on and reacted with substrates.
Key words: pulsed ion-beam, ablation plasma, thin film, crystalline, surface morphology

1. Introduction

In thin film preparation, adhesion is an important factor which is greatly related to property and life of the thin films. Since thin film and substrate are of different phases, there is a limit in adhesion. In order to obtain higher adhesion, the following methods can be used: (1) the increase in chemical adhesion or (2) formation of a mixing layer between the thin film and the substrate. The former can be observed by substrate heating and annealing, while the latter is obtained by an ion beam assisted deposition (IBAD) method [1]. However, substrate heating and annealing require extra cost. Furthermore, in the IBAD, the thickness of mixing layer obtained is about 100 nm, and in order to obtain a thicker mixing layer, it needs to add higher energy.

Irradiating an intense pulsed light ion-beam (LIB) onto a target causes formation of a high-temperature, high-density ablation plasma, and the plasma deposits on a substrate as a thin film. This process is called an intense pulsed light ion-beam evaporation (IBE) method [2-4]. Figure 1 shows outline drawing of the IBE method. Since the range of LIB is very short (for example the range of 1MeV proton (H^+) ion ~10μm for Aluminum), the energy of the ion beam is deposited in a very thin layer near the surface. Then the layer can be heated, melted, vaporized, ionized etc. As a consequence, high-density ablation plasma is produced to prepare thin films. Solid materials such as ceramic, metal or alloys, can be used as the targets for IBE.

When the plasma reaches the substrate, the plasma can give heat for the temperature increase in the thin film. In some combination of substrate and target, the maximum temperature can be as high as 900K, which could be raised by using substrates with low thermal conductivities [5]. This quick heating may enable us to react the substrate with plasma or melt the substrate. Utilizing the heat, we propose a novel thin film preparation method of simultaneous deposition and reaction process by IBE. As this example, this research was carried out to prepare Zr-Si compounds by depositing Zr thin films on Si substrates.

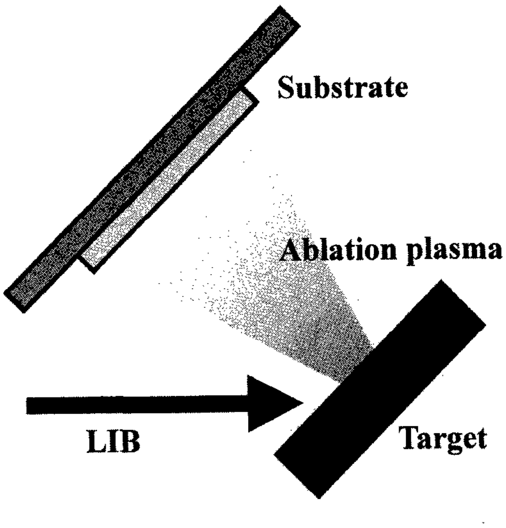

Fig. 1 Outline drawing of the IBE method.

2. Experiment al procedure

The experiment was carried out using an intense pulsed charged-particle beam generator, "ETIGO-II"[6]. Figure 2 shows the schematic of the experimental arrangement for the preparation of thin films by the IBE method. The left-hand side is the ion beam diode chamber that produces the LIB, while the right-hand side presents the thin film preparation chamber. The LIB was produced by a magnetically insulated diode (MID) [7] with a geometrically focused configuration. The MID consisted of an aluminum anode, on which the flashboard (1.5 mm-thick polyethylene) was attached as the ion source, and the cathode with slits to extract the ion beam. The gap distance between the anode and the cathode was 10 mm. To achieve geometric focusing of the beam, the anode and the cathode were shaped as concave structures with the curvature of 160 mm. The low-voltage, high-current flowing through the cathode from the external capacitor bank produced a transverse magnetic field (~0.5 T), which prevented the electrons from arriving at the anode. The beams were mainly composed of protons (>80%) and some carbon ions.

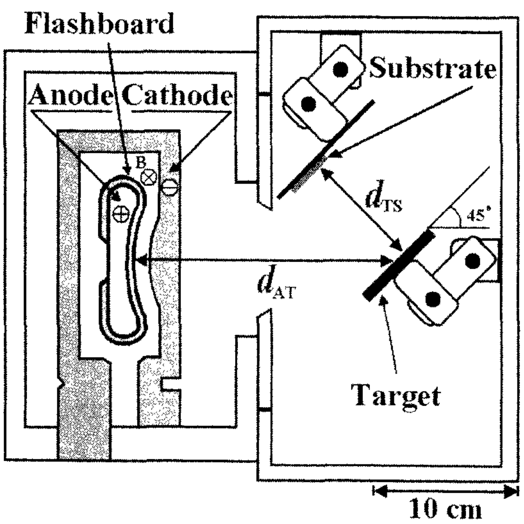

Fig. 2. Experimental setup of the IBE method.

Table I summarizes the experimental conditions. The target used was a metal Zr bulk (99.2%+Hf). This target was tilted at 45 ° to the beam axis. Si (100) single crystals were used as substrates. The energy density of the ablation plasma which reaches a Si substrate was changed by adjusting the distance from anode to target (d_{AT}) 200 mm from 180 mm, since the focus of the beam has been set as d_{AT}=160 mm and the energy density of the beam decreases with the increaser in d_{AT} above 160 mm. The energy densities of the LIB at the position of d_{AT}=200, 190 and 180 were 40, 45 and 50 J/cm^2 respectively. The thin films were prepared without substrate heating. The chambers were evacuated to 2x10^{-4} Torr. The phases in the thin films were estimated by X-ray diffraction (XRD). The cross-section of the thin film was observed by using scanning electron microscopy (SEM). Secondary electronic and back scattered electron images were both obtained.

Table I. Experimental conditions.

Main component of ions	Protons H^+(>80%)		
Target	Zr (99.2%+Hf)		
Substrate	Si (100)		
Sample	A	B	C
Energy density of the LIB [J/cm^2]	40	45	50
Distance from anode to target (d_{AT}) [mm]	200	190	180
Distance from target to substrate (d_{TS}) [mm]	60		
Target angle [deg.]	45		
Number of shots	1		
Substrate temperature ($T_{sub.}$)	RT		
Pressure [Torr]	2×10^{-4}		

3. Experimental results and discussion

3.1 Crystallity of the thin films

Figure 3 shows XRD patterns of samples A, B and C prepared at the above conditions. Only the peaks of Zr were observed in sample A. In sample B, not only the Zr peaks but also small peaks of $ZrSi_2$ were observed. This is considered to be the result of reaction between Si and Zr because the increase in the energy density of the LIB. In sample C, the intensity of $ZrSi_2$ peaks became higher than those in sample B. Moreover, in the sample C, the peaks of the poly-crystallization Si were also observed. Si substrates were single-crystal and any peaks other than Si (00ℓ) were observed before the experiment. From these results, the surface of Si substrate was melted by the high temperature plasma and was then re-crystallized.

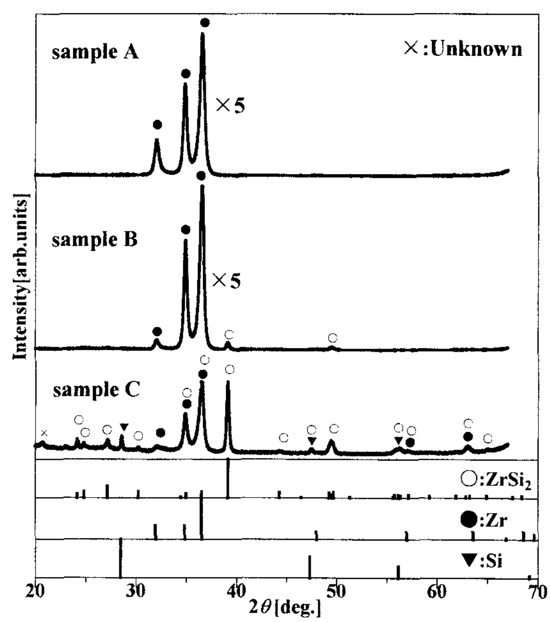

Fig. 3 XRD patterns of the Zr thin films prepared on Si substrates at the various d_{AT} conditions.

3.2 Cross-section of the thin films

Figure 4 shows cross-section SEM images of samples A, B and C by secondary electrons. In sample A, the uniform thin film with thickness of 300 nm was observed on a Si substrate. The interface between the thin film and Si substrate was clearly observed and straight. In sample B, a 300 nm-thick layer was present on the surface. Beneath the layer, some vertical cracks were seen and elongated to the depth of 1.0 μm. In sample C, the vertical cracks were also visible. In samples B and C, their interface between the thin films and the substrate were not clear and undulated.

The cross-section SEM images by back scattered electrons, at the same positions as Figs.4 (a)-(c) are shown in Figs. 5 (a)-(c). In sample A, the bright layer with thickness of 300 nm was seen on the surface, and there was an uniform dark potion under the layer. Since intensity in the back scattered electron image is proportional to the electron density in the sample, the bright layer consisted of heavy atoms [8]. From Fig.3, only Zr was detected in the thin film. Thus, the bright layer was Zr thin film, and the dark portion beneath the layer was the Si substrate. In sample B, the bright layer, which was similar to that in sample A, was also seen and must be Zr. Beneath the layer, bright and dark grains are seen in thickness about 1.0 μm. From Fig.3, this thin film contained Zr and $ZrSi_2$, which have higher electron density than that of Si therefore, the bright grains must be Zr or $ZrSi_2$, while the dark grains are of Si. In sample C, the morphology is similar to that in sample B. Thus the bright and dark grains were Zr or $ZrSi_2$ and Si, respectively. From Figs.3, 4 and 5, sample A has only Zr thin film on Si substrate, while the sample B and C have not only Zr but also mixed layer of $ZrSi_2$ and poly-Si grains.

As for these phenomena, the heat of ablation plasma is considered to be the cause. Si substrate surface heated by high-density, high-temperature ablation plasma [4] is melted, consequently Si reacts with deposited Zr and forms a compound of $ZrSi_2$. On the other hand, a part of liquid Si which did not react with Zr solidifies and poly-crystallizes.

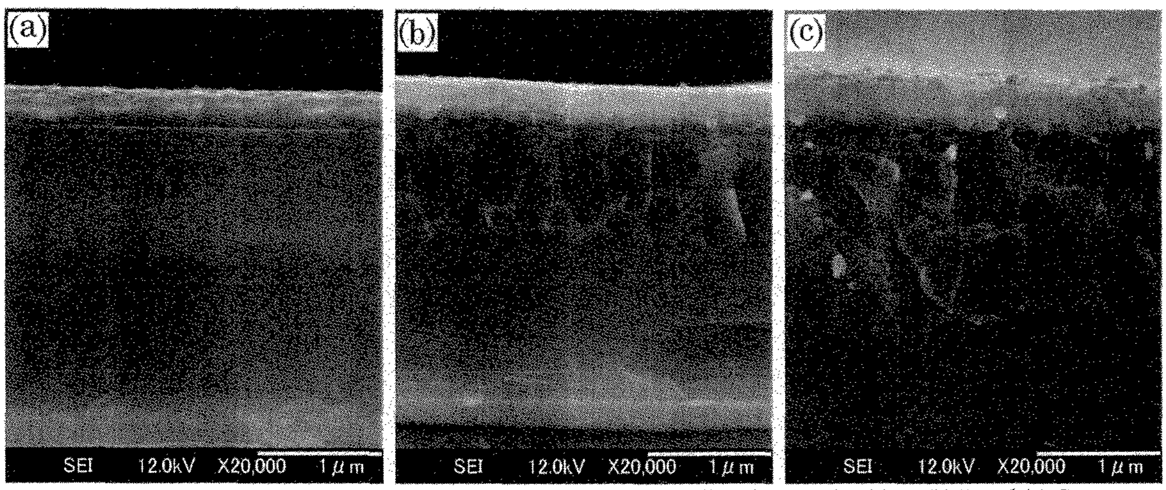

Fig. 4 Secondary electron images of cross-section of the thin films for samples (a) A, (b) B and (c) C.

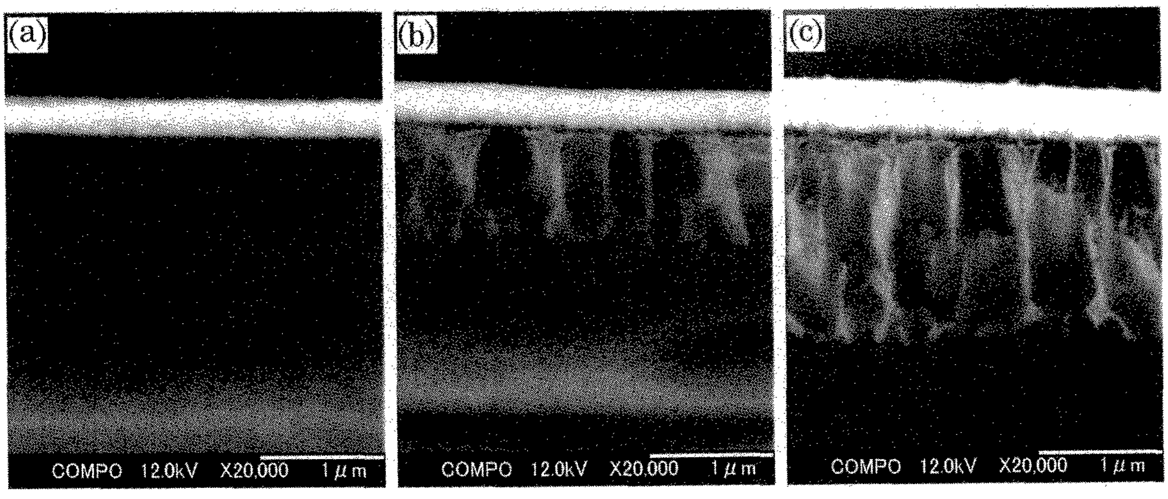

Fig.5 Back scattered images of cross-section of the thin films for samples (a) A, (b) B and (c) C.

4. Conclusion

Zirconium thin films were attempted to prepare by an intense pulsed ion-beam evaporation (IBE) method, and crystallinity and cross-section morphology of thin films were estimated. The following were concluded from the present experiments.

(1) Zr thin films are prepared on Si substrates and, not only Zr but also $ZrSi_2$ phases have been successfully prepared by using IBE method without substrate heating and annealing.

(2) The surface of Si substrates is melted by heat fluxing of plasma and reacted with Zr to form $ZrSi_2$ grains.

(3) This result demonstrated a possibility of simultaneous deposition and reaction process using an intense pulsed ion beam irradiation on a target.

5.Acknowledgemnts

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