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Ti-Al Alloy Films Synthesized by Ion-Beam-Enhanced Deposition†

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Abstract

Ti-Al thin films were prepared by ion beam enhanced deposition (IBED), where the films were prepared by depositing Ti and Al vapor and simultaneous bombardment with Ar ions in the energy range of 2-20 keV. Experiments were undertaken using a compact IBED system with a bucket-type 2.45-GHz electron-cyclotron-resonance ion source and an electron beam evaporation source. Results on the Rutherford backscattering spectrometry have suggested the presence of intermixing layer between substrate and Ti-Al film deposited with simultaneous bombardment with argon ions. X-ray diffraction patterns indicated the formation of $AlTi_3$, αTi(Al), βTi(Al) and amorphous-like phases. The phase structure could be determined by the Ar ion energy and the Ar/(Ti+Al) transport ratio.

KEY WORDS: (Ion beam enhanced deposition) (Ti-Al) (αTi) (βTi) ($AlTi_3$)

1. Introduction

Studies on ion beam enhanced deposition (IBED) have attracted great interest as a means of obtaining a wide variety of functional thin films to modify surface properties. In IBED at ion energies from several keV to several tens of keV, nuclear stopping is the dominant energy loss process for the bombarded ions in the growing film so that mixing effects, localized energy deposition in the collision cascade and rapid quenching of resultant energetic state (metastable phase) to ambient substrate temperature may be expected.[1-2] Experimental investigations on the IBED so far have been devoted primarily to the formation of nitride films.[3-6] Several studies on intermetallic alloy and/or compound formations during ion beam mixing of multilayered films using heavy ions with energies higher than 500 keV have been presented,[7-8] however, there have been few studies using IBED regime.

The intermetallic compounds in the Ti-Al system are of engineering significance as high-temperature materials because of their high melting temperature, good strength-to-weight ratio, high elastic modulus, strength up to elevated temperature, good creep resistance and susceptibility to high-temperature oxidation.[9-12] On the other hand, for the microelectronics applications an Al-transition-metal compound layer has been expected to significantly improve the electromigration capability.[13] In these applications, studies on alloy designing in terms of metallography, phase control and structural control of intermetallics are essential to obtain desirable properties.

Presented here are synthesis of Ti-Al intermetallic thin films by IBED, and discussions on ion-beam irradiation effects on their properties. The Ti-Al thin films are prepared by depositing Ti-Al vapor and simultaneous bombardment with Ar ions in the energy range of 2-20 keV.

2. Experimental Procedure

A compact IBED system [14] with a bucket-type 2.45-GHz electron-cyclotron-resonance (ECR) ion source and an electron beam (EB) evaporation source was used for the preparation of the Ti-Al films (**Fig. 1**). Acceleration voltage of the extracted Ar was varied in the energy range of 2-20 keV. The ion current measured using a Faraday cup with an entrance aperture of 3 cm in diameter was typically 1 mA; i.e., the ion current density onto substrate was 100 $\mu A/cm^2$. For characterization of the extracted ion beam, mass spectra of the extracted ions were measured using an analyzing magnet mounted on the other side of the ion source. **Figure 2** shows a typical example of the mass spectrum. The dominant ions were identified as

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Ar^+ with >95 at.% and Ar^{2+} with ~2 at.%.

The Ti-Al thin films were prepared on the Si (111) wafer by depositing the vapored titanium aluminide alloy (Ti:Al = 80:20 at%) with simultaneous bombardment with Ar ions. Using Rutherford backscattering spectrometry (RBS) the atomic percent of Al in the deposited film for the case of the Ti-Al alloy (Ti:Al = 80:20 at%) evaporation was measured to be ~30%, which was higher than the atomic percent of Al in the evaporated source because of lower melting temperature for Al than Ti.

The deposition rate of Ti-Al mixture atoms was measured with a quartz crystal monitor and was varied in the range of 1.5-4 Å/s. The base pressure of the deposition system, evacuated with a 1500-l/s cryopump, was $9x10^{-5}$ Pa. The working pressure of Ar during the ion source operation was $2\text{-}3x10^{-3}$Pa. The substrate temperature was controlled to be less than 250 °C by water cooling system.

The concentration and distribution of Ti and Al in the intermetallic phase was evaluated using RBS. The crystalline structure of the prepared films was investigated by glancing-angle x-ray diffraction (XRD) measurements performed at a grazing angle of 0.5-2°.

3. Results and Discussion

We performed experiments for preparation of Ti-Al thin films by depositing Ti-Al alloy with simultaneous bombardment with Ar ions. The thickness of intermixing layer between Si substrate and the growing film inferred from the RBS spectra of Ti was comparable to the Ar ion range calculated using TRIM code,[15] which was sufficiently less than the deposited film thickness.

Figure 3 shows the XRD patterns of the films prepared by 20-keV Ar ions at the Ar/(Ti+Al) transport ratio of 0.25-0.91. Shown also in Fig.3 is the XRD pattern of the as-deposited Ti-Al film indicating the amorphous phase. The crystalline structure changes from αTi(Al) phase to βTi(Al) phase with increasing Ar/(Ti+Al) transport ratio from 0.25 to 0.63, and at the Ar/(Ti+Al) transport ratio of 0.91 the film becomes amorphous-like structure. Furthermore for the films prepared at Ar/(Ti+Al) transport ratios of 0.63 and 0.91, broad peaks are observed in the diffraction angles of 25-30° and 35-45°. These broad peaks may indicate the formation of amorphous phase in Ti-Al system, however, further investigations are required for full understandings. Here the RBS analysis indicated that the film prepared at the Ar/(Ti+Al) transport ratio of 0.91 suffered considerable sputtering by Ar ion bombardment and the resulted film thickness was less than 1/10 of the expected Ti-Al thickness measured with the crystal monitor.

The XRD patterns of the films prepared by 2-10 keV Ar ions are shown in **Fig. 4**. The films prepared with 2-keV ion beam indicate the formation of $AlTi_3$ phase at the Ar/(Ti+Al) transport ratio of 0.29 and the broad peak of βTi(Al) phase above 0.55. Here it should be noted that high-resolution TEM may be necessary for the interpretation of the broad peaks in Figs. 3 and 4 as "amorphous" or "microcrystalline" state. Comparison of the deposited films with ion energies of 2-10 keV at the nearly constant Ar/(Ti+Al) transport ratio of 0.5 suggests the change in preferred grain texture from the βTi(Al) (200) to the βTi(Al) (110) with increasing ion energy. Further investigations, however, are necessary to describe the mechanism for the change in the preferred crystallographic orientation tilted from the film plane.

The results obtained with the XRD patterns in Figs.3 and 4 are summarized in the phase structure of Ti-Al films shown in **Fig. 5** as a function of the energy of Ar ions and the Ar/(Ti+Al) transport ratio. This result indicates that the phase structure may be controlled by the beam energy and predominantly by the transport ratio. In the transport ratio below about 0.4, $AlTi_3$ phase changes

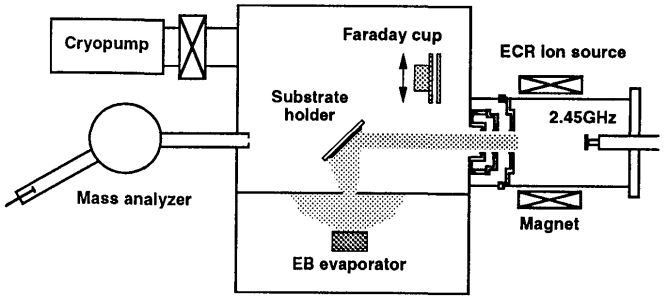

Fig. 1 Schematic of IBED system.

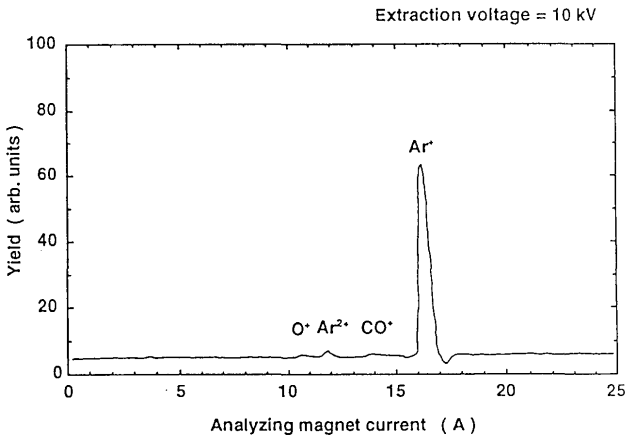

Fig. 2 Typical mass spectrum of ions. This example was measured for an acceleration voltage of 10 kV.

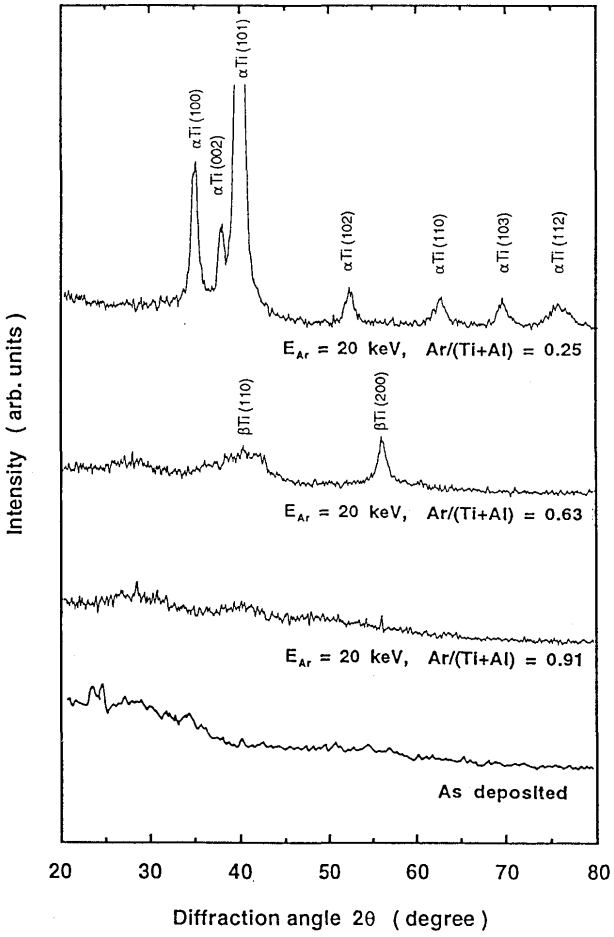

Fig. 3 XRD patterns of the Ti-Al films prepared with 20-keV Ar ion beam at the Ar/(Ti+Al) transport ratios of 0.25-0.91. Shown also is the XRD patterns of a as-deposited Ti-Al film for comparison.

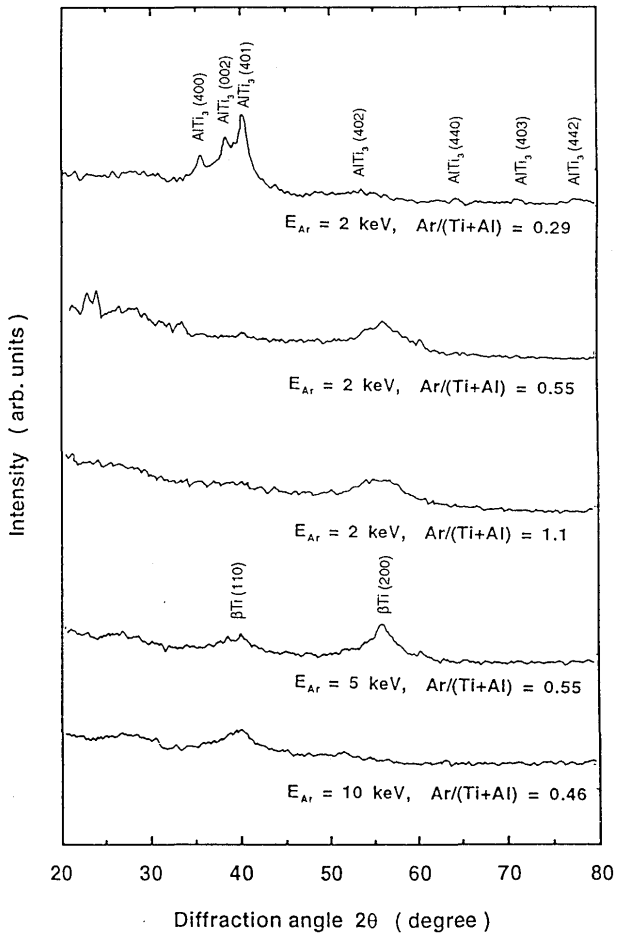

Fig. 4 XRD patterns of the Ti-Al films prepared with 2-10 keV Ar ion beam at the Ar/(Ti+Al) transport ratios of 0.29-1.1.

to αTi(Al) phase with increasing beam energy. It should be pointed here that $AlTi_3$ has an ordered hexagonal structure based on αTi(Al) and is also designated α_2 phase [16]. The βTi(Al) phase is formed in the medium transport ratio above Ar/(Ti+Al) > 0.4, however, the boundary between the βTi(Al) phase and the amorphous-like phase seems to be more dependent on the beam energy.

One possible interpretation of this phase structure may be undertaken by analogizing it with the equilibrium solid phase diagram of the Ti-Al system [16]. Here it should be noted that the atomic percent Al in the film prepared by the Ti-Al alloy (Ti:Al = 80:20 at%) evaporation was measured to be ~30% from the RBS analysis. At this atomic content of Al, the $AlTi_3$ with an ordered hexagonal structure is formed below about 1180 °C, the cph αTi(Al) solid solution is formed in the temperature range of 1180-1210 °C, in the temperature range of 1210-1650 °C the bcc βTi(Al) phase is formed, and the liquidus temperature is about 1650 °C.[16] In the phase structure

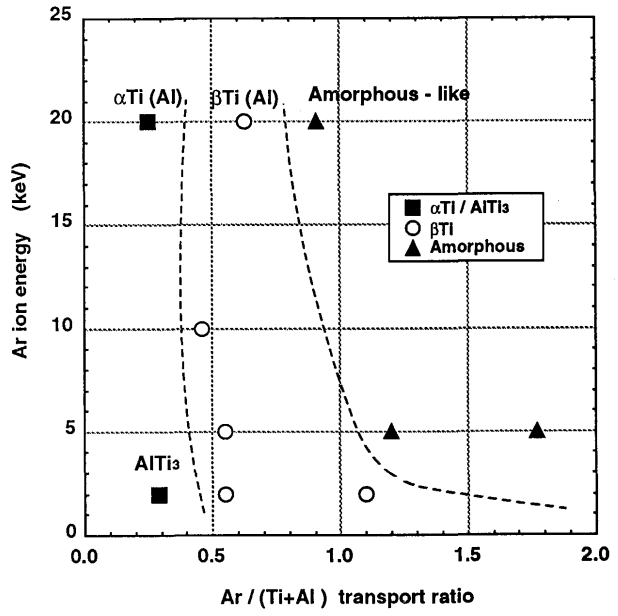

Fig. 5 The phase structure of Ti-Al films as a function of the Ar ion energy and the Ar/(Ti+Al) transport ratio.

shown in Fig.5, the average kinetic energy per a deposited Ti or Al atom transferred from incident Ar ions through the collision cascade becomes larger with increasing ion energy or with increasing Ar/(Ti+Al) transport ratio. From this point of view, $AlTi_3$, αTi(Al), βTi(Al) and amorphous-like phases observed in Fig.5 seem to appear in the order of increase in the average kinetic energy of deposited atoms transferred from the incident Ar ions, which is consistent with the stability of the phases in the crystalline phase in the equilibrium Ti-Al system. This analogy suggests that the quasi-high energetic state formed in the collision cascade is rapidly quenched to the ambient temperature within the duration of the collision cascade (<< 1 ns) so that the high temperature phase is *frozen* at the substrate temperature.

4. Conclusion

Ti-Al films were prepared by depositing Ti-Al vapor deposition and simultaneous bombardment with Ar ions in the energy range of 2-20 keV. XRD patterns of the Ti-Al films prepared by Ti-Al vapor deposition and simultaneous bombardment with Ar ions indicated the formation of $AlTi_3$, αTi(Al), βTi(Al) and amorphous-like phases. The phase structure of the Ti-Al system prepared with Ar ion beam could be controlled by the combination of the ion beam energy and the Ar/(Ti+Al) transport ratio.

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