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M. Takahashi, F. Kanamaru, M. Harada, I. Watanabe. Crystal and Electronic Structures and the Corrosion Resistance for Metal Nitrides in the TiN-AlN System. Journal de Physique IV Proceedings, 1997, 7 (C2), pp.C2-1215-C2-1216. 10.1051/jp4:19972200 . jpa-00255272

HAL Id: jpa-00255272

<https://hal.science/jpa-00255272>

Submitted on 1 Jan 1997

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Crystal and Electronic Structures and the Corrosion Resistance for Metal Nitrides in the TiN-AlN System

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Both aluminum and titanium *K*-edge XAFS spectra of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ ($0 \leq x \leq 1.0$) films were measured to investigate the corrosion resistance of compounds in the TiN-AlN system. Analyses of both Al and Ti *K*-XAFS revealed that both Ti and Al atoms occupy the octahedral site in the NaCl-type $\text{Ti}_{1-x}\text{Al}_x\text{N}$ ($0 \leq x \leq 0.58$) and the tetrahedral site in both the würtzite-type $\text{Ti}_{1-x}\text{Al}_x\text{N}$ ($0.83 \leq x \leq 1.0$) and the intermediate phase ($x \approx 0.7$). Ti *K*-XAFS of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ films annealed in O_2 gas flow and aged in distilled water were also measured by employing the helium ion yield technique with a small angle incidence. The XANES spectrum of annealed TiN film shows the pre-edge feature, which is observed for rutile phase TiO_2 and such feature is not appreciably observed for NaCl-type $\text{Ti}_{1-x}\text{Al}_x\text{N}$'s and merely observed for the intermediate phase and würtzite-type $\text{Ti}_{1-x}\text{Al}_x\text{N}$'s. It has been found from the XANES spectra that $\text{Ti}_{1-x}\text{Al}_x\text{N}$ ($x=0.9$) is oxidized in water and Al_2TiO_5 is produced while TiN and $\text{Ti}_{1-x}\text{Al}_x\text{N}$ ($x \leq 0.8$) is hardly oxidized. Results of the XPS measurements and the DV-X α MO calculations are also discussed.

1. INTRODUCTION

TiN has been used for hard coatings for machining operations, diffusion barrier layers for electronic device fabrications, and so on. In order to improve properties of TiN coatings, the addition of other metal to TiN has been examined by many researchers and it has been found that $\text{Ti}_{1-x}\text{Al}_x\text{N}$ films is not oxidized below 900°C in air[1] and seem to provide a promising alternative to TiN films[2]. Such high oxidation resistance of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ has been thought to be due to the formation of a bilayer oxide composed of two sublayers[3]. Owing to the small sample volume and the highly defective nature of the oxide layers, however, there was too few crystallographic information on the layers. In the present work the He ion yield XAFS technique[4] with a small incidence angle is used to allow Ti *K*-XAFS measurements to be sensitive to the surface layer. The technique is applied to the local structure investigation on the oxidized layer of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ films. Ti *K*- and Al *K*-XAFS were also measured for as-deposited films to obtain information on the local structure around both Ti and Al for the solid solutions.

2. EXPERIMENTAL

$\text{Ti}_{1-x}\text{Al}_x\text{N}$ films were prepared using the rf-magnetron sputtering apparatus under the mixed gas atmosphere, comprising Ar and N_2 . Metal composites formed by Al tips on Ti disk or Ti tips on Al disk were used as the target. Films were grown onto a polycrystalline alumina substrate and a polystyrene film, coated on a glass slide for Ti *K*-XAFS and Al *K*-XAFS measurements, respectively. The polystyrene substrate deposited films was sunk in THF to separate product film from the glass slide and the film was washed three times by THF to remove polystyrene. Annealing of deposited films was carried out in flowing pure O_2 for 10min. Each one piece of as-deposited films was dipped into distilled water for 2 weeks. As-deposited and oxidized films and films peeled off from a glass slide were stored in *n*-hexane to prevent surface oxidation.

Al *K*-edge XAFS spectra were measured at the BL-7A in UVSOR of Institute for Molecular Science in Okazaki with 750MeV electrons. The two-crystal monochromator of a beryl was used and the photon energy was calibrated using Al metal powder. The sample, mixed with active carbon in *n*-hexane, were applied on the first dinode of the electron multiplier. I_0 was monitored by the gold mesh transmitting 80% of photons and the total electron yield was recorded. The conversion electron yield method under atmospheric He gas flow[4] was used to measure Ti *K*-XAFS of the films at BL-12C in the Photon Factory of the National Laboratory for High Energy Physics in Tsukuba, with 2.5GeV electrons. The incident X-ray was monochromatized with Si(111) double crystals and focused by the mirror, and the higher harmonics were rejected using a quartz mirror in He gas flowing. An incidence angle of the sample was varied by the computer-controlled precision stage. The experimental setup for the He ion yield XAFS measurements has been described elsewhere[4].

3. RESULTS and DISCUSSION

Figure 1 shows the normalized Ti *K*-XAFS spectra of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ films before and after annealed in flowing O_2 . The dashed line depicts as-deposited films. Spectra of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ ($x \leq 0.3$) have small pre-edge peak and rather intense white line, while those with $x \geq 0.7$ shows intense pre-edge peak, indicating that Ti is tetrahedrally coordinated by four N atoms in $\text{Ti}_{1-x}\text{Al}_x\text{N}$ ($x \geq 0.7$). On the other hand, Ti-rich $\text{Ti}_{1-x}\text{Al}_x\text{N}$'s take the same coordination state for Ti as that in TiN, i.e., Ti is octahedrally coordinated by six N atoms. These coincide with findings by the XRD measurements that $\text{Ti}_{1-x}\text{Al}_x\text{N}$ crystallizes in three crystal phases with Al content, *x*, i.e., NaCl-type solid solution with $0 < x \leq 0.58$, würtzite-type solid solution with $0.83 \leq x < 1.0$ and an intermediate phase belonging to the hexagonal system in the vicinity of $x = 0.7$. In the Al *K*-edge XANES spectrum for AlN

a sharp absorption peak is found at 1.5628 keV and another peak is located at 1.5687 keV. The spectral shape for $Ti_{1-x}Al_xN$ ($x=0.8$) closely resembles that for AlN. The position of the peak around 1.563keV slightly shifts to higher energy side and becomes weaker and broader for $Ti_{1-x}Al_xN$ ($x=0.7$). Thus the local structure around Al in the würtzite-type solid solution resembles to that for AlN, i.e., Al occupies the tetrahedral site, and as for $Ti_{1-x}Al_xN$ ($x\approx 0.7$) the coordination and the electronic states for Al somewhat differ from those for AlN, though the phase takes the structure which resembles to the würtzite-type one. The XANES spectra for the NaCl-type solid solutions are completely different from that for AlN, suggesting that Al no more occupies the tetrahedral site. The position of the pre-edge peak at both Ti and Al K-XANES shifts to lower energy side with increasing Al content, corresponds to the findings, obtained by XPS measurements, that the highest occupied level shifts to higher binding energy side with an increment of Al.

An oxidation at 600°C under O_2 gas flow makes TiN into rutile phase TiO_2 as shown in Figs.1(a) and (b). The intensity of the pre-edge peak around 4.968keV for NaCl-type $Ti_{1-x}Al_xN$ increases with the oxidation at 600°C and so does for TiN oxidized at 400°C. In addition the intensity around 4.99keV, where the dip is observed for spectra of as-deposited films, increases after the annealing at 600°C. These findings indicate that the oxidation causes a partial oxidation of the film surface and the product oxide is TiO_2 -like species. $Ti_{1-x}Al_xN$ ($x\approx 0.7$) is also oxidized partially at 600°C, while würtzite-type $Ti_{1-x}Al_xN$'s hardly oxidized, though no oxidation has been detected for $Ti_{1-x}Al_xN$ ($0 < x \leq 1$) by the TG analyses[1]. The fact

that würtzite-type $Ti_{1-x}Al_xN$'s are rarely oxidized seems to be caused by the large covalency, which results in the intense pre-edge peak. The DV-X α MO calculations for TiN and NaCl-type solid solutions implies that the increment of covalency of the metal-metal bond with the substitution of Al for Ti leads to the improvement of the durability against oxidation, which is consistent with the present XAFS measurements. Slightly thick surface oxide layer is found in XPS of these films as compared with those of corresponding as-deposited films, showing the present technique for the XAFS measurement is valid for the detection of the surface oxidation of the film.

By aging in distilled water, $Ti_{1-x}Al_xN$ ($x=0.9$) is almost changed to Al_2TiO_5 , while both TiN and NaCl-type $Ti_{1-x}Al_xN$ is hardly oxidized, as shown in Fig. 2. An existence of a little amount of TiO_2 is observed for $Ti_{1-x}Al_xN$ ($x=0.7$ and $x=0.8$). These findings suggest that the water resistance for AlN is improved with an addition of Ti but a considerable dose of Ti is required.

Acknowledgements

This work has been performed under the approval of the Photon Factory Program Advisory Committee (Proposal No. 95-G220) and the Joint Studies Program (7-843) of UVSOR, IMS.

Fig.1 Ti K-XAFS spectra for $Ti_{1-x}Al_xN$ and TiO_2 films and Al_2TiO_5 powder. (a) TiO_2 , (b)TiN, (c) $x=0.1$, (d) $x=0.3$, (e) $x=0.7$, (f) $x=0.8$, (g) $x=0.9$, and (h) Al_2TiO_5 . As-deposited films are plotted by a broken line. A solid line shows films annealed at 600°C and an alternative long and short dash line depicts TiN oxidized at 400°C.

Fig.2 Ti K-XANES spectra for $Ti_{1-x}Al_xN$ and TiO films and Al_2TiO_5 powder. (a) TiO_2 , (b)TiN, (c) $x=0.1$, (d) $x=0.7$, (e) $x=0.8$, (f) $x=0.9$, and (g) Al_2TiO_5 . A solid line indicates films soaked in distilled water for 2 weeks. As-deposited films are displayed by a broken line.

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