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The Preparation of NaCl-Type $Ti_{1-x}Al_xN$ Solid Solution

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$Ti_{1-x}Al_xN$ solid solutions ($0 \leq x < 0.6$) with NaCl-type structures were synthesized by a rf-sputtering method. The lattice constant of the solid solutions linearly decreases with increasing Al content. For samples with x greater than 0.5, a remarkable lattice distortion was observed.

Introduction

Titanium nitride with a NaCl-type structure exhibits electrical conductivity in the metallic range, whereas aluminum nitride with a wurtzite-type structure is well known as a dielectric substance with a wide band gap of about 6eV. Both materials have also been spotlighted as high-temperature materials.

Recently, the ternary system Ti–Al–N has been investigated by Schuster and Bauer (*1*) who encountered three different crystal phases with N/(Ti + Al) ratios smaller than unity: Ti_2AlN, denoted as the H phase; Ti_3AlN, with the perovskite-type structure; and $Ti_3Al_2N_2$, included in the hexagonal system. On the other hand, a few reports (*2, 3*) have been presented on the binary system TiN–AlN. The products are not single phase, but mixtures of TiN and amorphous AlN, or of TiN and crystalline AlN. The difficulty of forming solid solutions in the TiN–AlN system is due to large differences in both crystal structure and chemical bonds between TiN and AlN; both Ti and N atoms in TiN have coordination numbers of 6, while in AlN the coordination numbers of Al and N atoms are 4.

In this work, a co-sputtering method was applied for preparing the solid solutions in the system TiN–AlN. Some crystallochemical characterizations of the vapor-deposited $Ti_{1-x}Al_xN$ with NaCl-type structure are described in the present paper.

Experimental

The rf-magnetron sputtering apparatus used for the preparation of $Ti_{1-x}Al_xN$ films was an ANELVA SPF-210H type. The targets used for co-sputtering were composed of an Al disk (100 mm Φ) and Ti chips (5×5 mm^2) geometrically arrayed on the Al disk. Nitride films with a thickness of 1 μm were fabricated on glass slide substrates by reactive co-sputtering in an equimolar gas mixture of Ar and N_2. Sputtering conditions are shown in Table I. The chemical composition of the sputtered films was controlled by varying the Ti coverage on the Al target.

The X-ray diffraction patterns of the as-sputtered films were taken by a powder diffractometer, Rigaku RAD-RB, with graph-

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TABLE I

RF-MAGNETRON SPUTTERING CONDITIONS FOR THE FILM PREPARATION

Target	Ti chips on Al disk
Substrate	Slide glass
Sputtering gas	Ar + N_2 (1 : 1)
Gas pressure	1×10^{-2} Torr
Rf power	100 W
Rf frequency	13.56 MHz
Magnetic field	100 G

ite monochromatized CuKα radiation, and the Bragg angle was calibrated using Si powder as a standard. The chemical composition of the films was determined by using an analytical electron microscope (AEM), HU-12SE, which has a spatial resolution of 30 nm for microanalysis. Aluminum titanate, Al_2TiO_5, was used as a standard material for quantitative analysis by AEM. Nitrogen content in the films was evaluated by ESCA spectroscopy, PERKIN-ELMER PHI 5100, using gold-colored TiN prepared in the present study as a standard.

Results and Discussion

The Ti/Al ratio in the sputtered films, which was determined by AEM measurement, is lower by a factor of 1.4 ± 0.3 than the area ratio of Al to Ti on the targets. The ratio of N to metal atoms [$(1 - x)$Ti + xAl] was estimated to be almost unity by means of ESCA spectroscopy. From the results of AEM and EM measurements, it was also confirmed that each of the $Ti_{1-x}Al_xN$ films with $0 \leq x \leq 0.58$ had good homogeneity in both chemical composition and texture. In order to check oxygen contamination, Auger electron spectroscopy was carried out on the sputtered films. The Auger electron spectra of the TiN films before and after etching the film surface are displayed in Figs. 1a and 1b, respectively. The spectrum (a) suggests that the surface of the sputtered film is appreciably oxidized. While, after etching the film surface with an argon ion beam, little oxygen signal is observed as shown in Fig. 1b, indicating that oxygen contamination had not occurred during film deposition.

The TiN films, prepared at a gas pressure of 1×10^{-2} Torr, were gold in color and exhibited an X-ray diffraction pattern corresponding to NaCl-type structure, and the preferred orientation with the (100) plane being parallel to the film surface was observed as shown in Fig. 2a. The solid solutions in the composition range of $0.13 \leq x \leq 0.58$ were dark greenish brown in color and the X-ray diffraction patterns of them also show remarkable preferred orientation as shown in Figs. 2b and 2c.

To clarify the structure type of the solid solutions, both X-ray and electron diffraction photographs of the powder samples scrapped from the substrate were taken. All diffraction lines observed in each sample were indexed with a NaCl-type lattice.

Figure 3 displays rocking curves of the

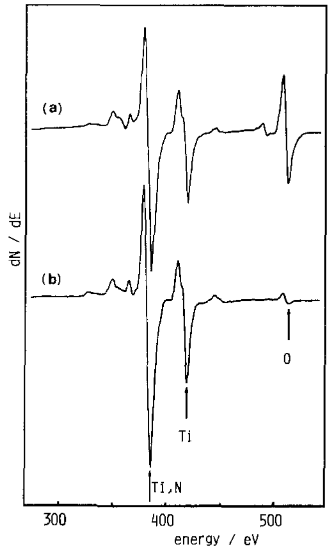

FIG. 1. Auger electron spectroscopy of the TiN film: (a) as-sputtered films, (b) after etching.

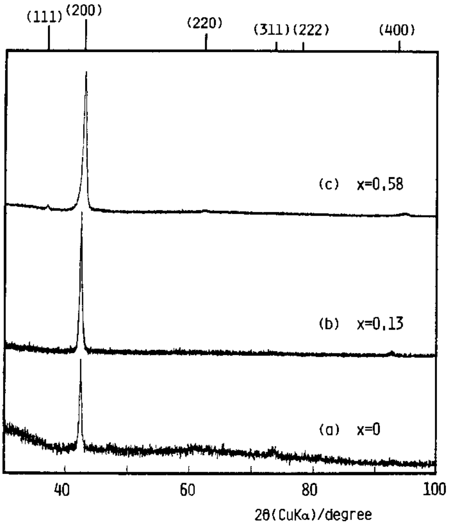

FIG. 2. X-ray diffraction patterns of $Ti_{1-x}Al_xN$ with NaCl-type structure (sputtered at gas pressure 1×10^{-2} Torr).

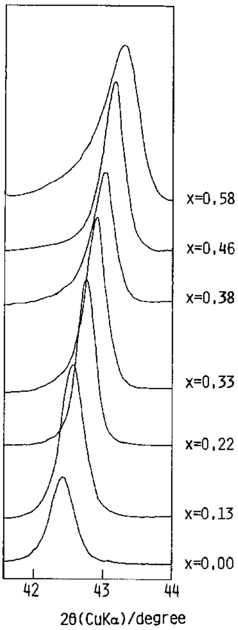

FIG. 3. X-ray diffraction profiles near (200) reflection of the NaCl-type phase.

200 reflection of the $Ti_{1-x}Al_xN$ solid solutions with NaCl-type structure, which were prepared under the gas pressure of 1×10^{-2} Torr. The 200 diffraction peak shifts toward a higher Bragg angle with increasing Al content. For the films with $x = 0.61$ an unidentified crystal phase crystallized with the NaCl-type phase. The relationship between the chemical composition, x, and the lattice constant calculated using the 200 and 400 reflections is represented in Fig. 4. The lattice constant of NaCl-type solid solutions linearly decreases with increasing Al content. In the films with $x = 0$, the lattice constant of the film obtained at a sputtering gas pressure of 1×10^{-2} Torr was a little larger than that of ASTM card 6-0644.

The 200 reflection of the as-sputtered film with $x = 0.58$ is broad and asymmetric as shown in Fig. 3. However, after annealing the films at 400°C in N_2 gas, the rocking curve of the 200 reflection remarkably became sharp and symmetric compared with that of the as-sputtered films. As mentioned above, the results of AEM and EM measurements on the as-sputtered film showed that the film had good homogeneity in both chemical composition and texture as well

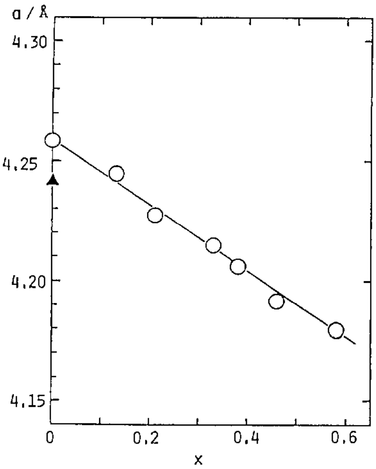

FIG. 4. Relationship between lattice constant and composition of $Ti_{1-x}Al_xN$ with NaCl-type structure. ○: sputtered films at gas pressure 1×10^{-2} Torr, ▲: reported value at ASTM card 6-0644.

as the films with $x \leq 0.46$. These findings suggest that the sputtered film with $x = 0.58$ is also a single phase with NaCl-type structure.

The electric resistivity of TiN is 2.5×10^{-5} Ω cm at room temperature while those of NaCl-type solid solutions were 4×10^{-4} Ω cm for $x = 0.13$ and 5×10^{-2} Ω cm for 0.58, respectively. The electric resistivity of NaCl-type solid solutions increased with increasing Al content.

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