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Preparation and properties of $Al_{1-x}Ti_xN$ solid solution thin films by multiple cathode sputtering

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Abstract

$Al_{1-x}Ti_xN$ solid solution thin films were deposited by reactive sputtering of a multi-metal target. A wurtzite-type solid solution was obtained in $x=0$–0.3, and an NaCl-type solid solution was obtained in $x=0.4$–1.0. Optical and electrical properties varied with composition x. The binding energies of Ti2p, Al2p and N1s from XPS spectra shifted remarkably between $x=0.3$ and 0.4. The improvement of the oxidation resistance of the Al substituted TiN films and aluminum-rich oxide formation near the film surface was observed by XPS depth profiles. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Films; Nitrides; Optical properties; Oxidation resistance; Spectroscopy

1. Introduction

Aluminum nitride (AlN) has a wurtzite crystal structure and is a semiconductor with a wide energy gap of about 6 eV, and is also noted as a piezoelectric material that exhibits a high acoustic velocity. Titanium nitride (TiN) has an NaCl-type crystal structure and exhibits a metallic conduction. Recently, aluminum-doped TiN, due to its anti-oxidation property, is gaining attention for application to an intermediate layer between a poly-Si plug and a capacitor in an advanced memory device.[1–3] In this paper, $Al_{1-x}Ti_xN$ solid solution thin films were deposited by reactive sputtering of a multi-metal target. Their structure, and their optical and electrical properties, and their oxidation resistance were measured and discussed.

2. Experimental

$Al_{1-x}Ti_xN$ solid solution thin films were deposited by a planar rf magnetron sputtering with a multi-metal target. The Al (99.999%) and Ti (99.99%) metal targets were located at 180° intervals. The substrates were fixed to a rotary-type substrate holder through a load-lock chamber. Before the gases were introduced to the sputtering chamber, the entire system was evacuated to a pressure of about 5×10^{-5} Pa. In this experiment, an IR heater was not used in order to obtain solid solution films. The sputtering conditions are shown in Table 1. The film thickness was estimated to be 300–400 nm.

The chemical composition of the films was determined by an X-ray fluorescence analysis and XPS. The optical transmittance of a film on the quartz substrate in the wavelength range from 190 to 850 nm was measured with a dual beam spectrophotometer. The IR transmittance of the films on the (100) Si wafer was measured using a Fourier-transform spectrophotometer (FTIR). The electrical resistivity of the films was determined by Van der Pauw method. The binding energies of Ti2p, Al2p and N1s were measured by means of XPS (Rigaku X7000) with MgK_α X-ray radiation below 10^{-6} Pa. Before measurement, Ar ion etching was carried out to remove the surface oxidized layer, and a low energy electron gun was used to stabilize the surface potential on insulating materials. The photoelectron spectra were calibrated by an $Au7f_{7/2}$ peak of 83.8 eV. The depth profiles of the annealed films were measured by XPS (Surface Science Instruments S-Probe ESCA 2703) with AlK_α X-ray radiation.

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3. Results and discussion

Fig. 1 shows X-ray diffraction patterns of $Al_{1-x}Ti_xN$ films. The structure of the deposited films were classified into the following two phases: *C*-axis-oriented wurtzite or a related structure with $x = 0$–0.30, and (111)-oriented NaCl-type solid solution with 0.40–1.0. The lattice constant in the NaCl structure followed Vegard's Rule.

The colors of the deposited films were transparent in $x = 0$, translucent and yellow brown in $x = 0.005$–0.3, brownish silver with a metallic luster in $x > 0.4$. Fig. 2 shows the optical transmittance of the deposited $Al_{1-x}Ti_xN$ films on fused quartz substrates. The absorption edge shifted to the higher wavelength side with increasing x, indicating that the optical band gap became narrower by the Ti substitution in the AlN lattice.

Table 1
Sputtering conditions

Target	Al (99.999%), Ti (99.99%)
Substrate	Corning No. 7059 glass, Fused quartz, Si
Substrate temperature	Ambient
Sputtering gas	$Ar{:}N_2 = 1{:}1$
Gas pressure	1.2 Pa
RF input power	0–400 W
Substrate rotation	11.25 rpm

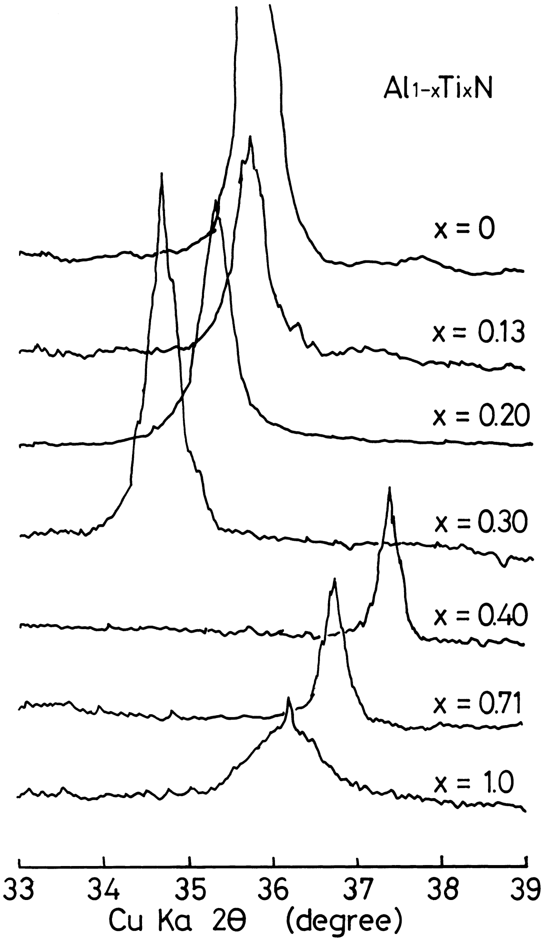

Fig. 1. X-ray diffraction patterns of $Al_{1-x}Ti_xN$ ($0 \leqslant x \leqslant 1.0$) thin films on Corning No. 7059 glass substrates.

The lattice vibration spectra of $Al_{1-x}Ti_xN$ films on Si substrates are shown in Fig. 3. The absorption peak around 670 cm^{-1} in $x = 0$ corresponds to the frequency of the transverse modes of the optical phonons at the center of the Brilloin zone in AlN.[4,5] The absorption peaks became more broad and shifted to the lower wavelength side, indicating that the frequency of the phonon, and probably the sound velocity also, decreased with increasing of Ti content in the AlN structure. NaCl-

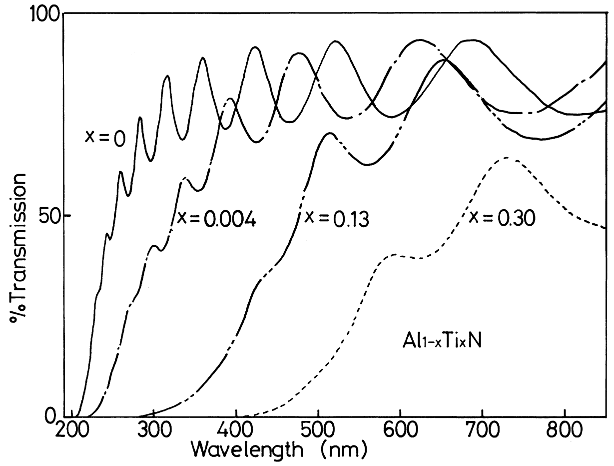

Fig. 2. Optical transmittance of $Al_{1-x}Ti_xN$ ($0 \leqslant x \leqslant 0.30$) thin films on fused quartz glass substrates.

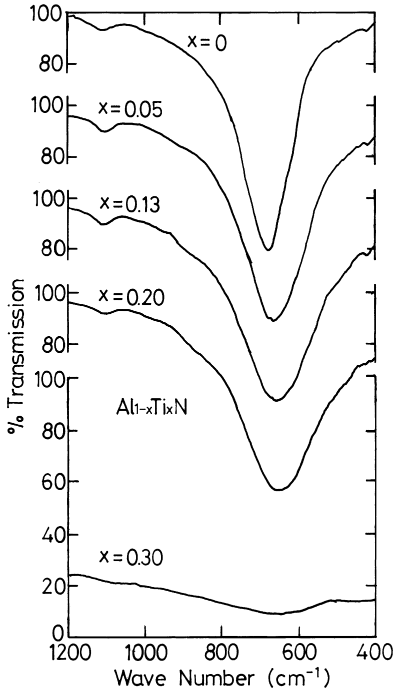

Fig. 3. The IR transmittance spectra of $Al_{1-x}Ti_xN$ ($0 \leqslant x \leqslant 0.30$) thin films on Si substrates for normal incidence.

type $Al_{1-x}Ti_xN$ films were not transparent to the infrared light.

Values for temperature dependence of resistivity are shown in Fig. 4. With increase of Al contents, the resistivity increased, and the temperature coefficient decreased from positive in $x=1$ through to zero in $x=0.87$ to negative. Wurtzite $Al_{1-x}Ti_xN$ films had a value of resistivity too high to be measured by dc four probe methods.

The electron binding energies of Ti2p, Al2p and N1s measured by XPS are shown in Fig. 5. As can be seen in the figures, the peaks shifted remarkably between $x=0.3$ and 0.4. This shift is concomitant with the change in crystal structure. In AlN, both Al and N have coordination numbers of 6, while in TiN, Ti and N have coordination numbers of 4. In $x=0.4$, the Ti2p photoemission peak shifted to 1.0 eV, on the lower binding energy side, as compared to the peak in $x=0.3$. Conversely, both Al2p and N1s peaks shifted to 0.4 eV, on the higher binding energy side. These results indicate that Ti in the NaCl structure is electron poorer than Ti in the wurtzite structure, and that Al and N in NaCl structure are more electron rich than the corresponding elements in the wurtzite structure. Charge transfers from Al and N to Ti occur when the crystal structure changes from a wurtzite to an NaCl structure. The binding energy shifts in the region of $x=0$–0.3 and in the region of $x=0.4$–1.0 are not so drastic. Therefore, the resistivity changes in the NaCl-type films ($x=0.4$–1.0) are difficult to explain by using the measured XPS data; they are probably related to the structural changes in electrons close to their Fermi level.

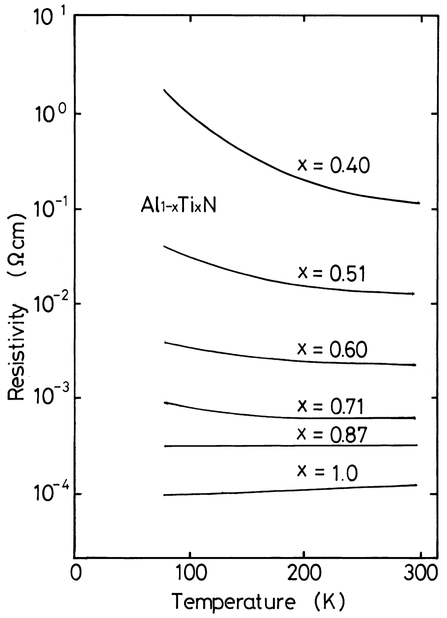

Fig. 4. Temperature dependence of resistivity of $Al_{1-x}Ti_xN$ ($0.40 \leqslant x \leqslant 1.0$) thin films on Corning No. 7059 glass substrates.

The oxidation resistance of the NaCl-type films ($x=0.4$, 0.71 and 1.0) was analyzed by XPS depth profiles. The results are shown in Fig. 6. These films were annealed in pure oxygen for 10 min. In TiN ($x=1.0$), estimated oxide thickness was about 150 nm, while in the film with $x=0.4$ and 0.71, the estimated oxide thickness was about 40nm, showing that the oxidation resistance was improved by Al substitution. It is also noted that Al diffusion to the surface was seen in the film with $x=0.71$. This cation segregation is believed to be responsible for the high oxidation resistance.[2,3] In our results, the oxidation resistance of the films with $x=0.4$ and 0.71 are almost identical, suggesting that

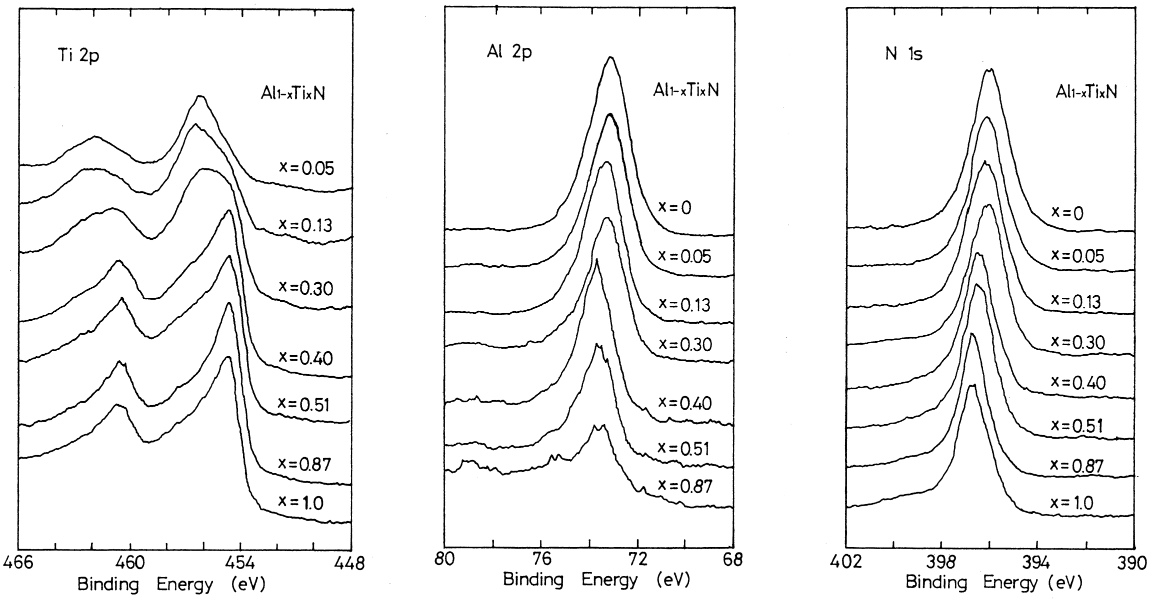

Fig. 5. Photoemission peaks obtained from $Al_{1-x}Ti_xN$ ($0 \leqslant x \leqslant 1.0$) thin films. (a) Ti2p, (b) Al2p, and (c) N1s.

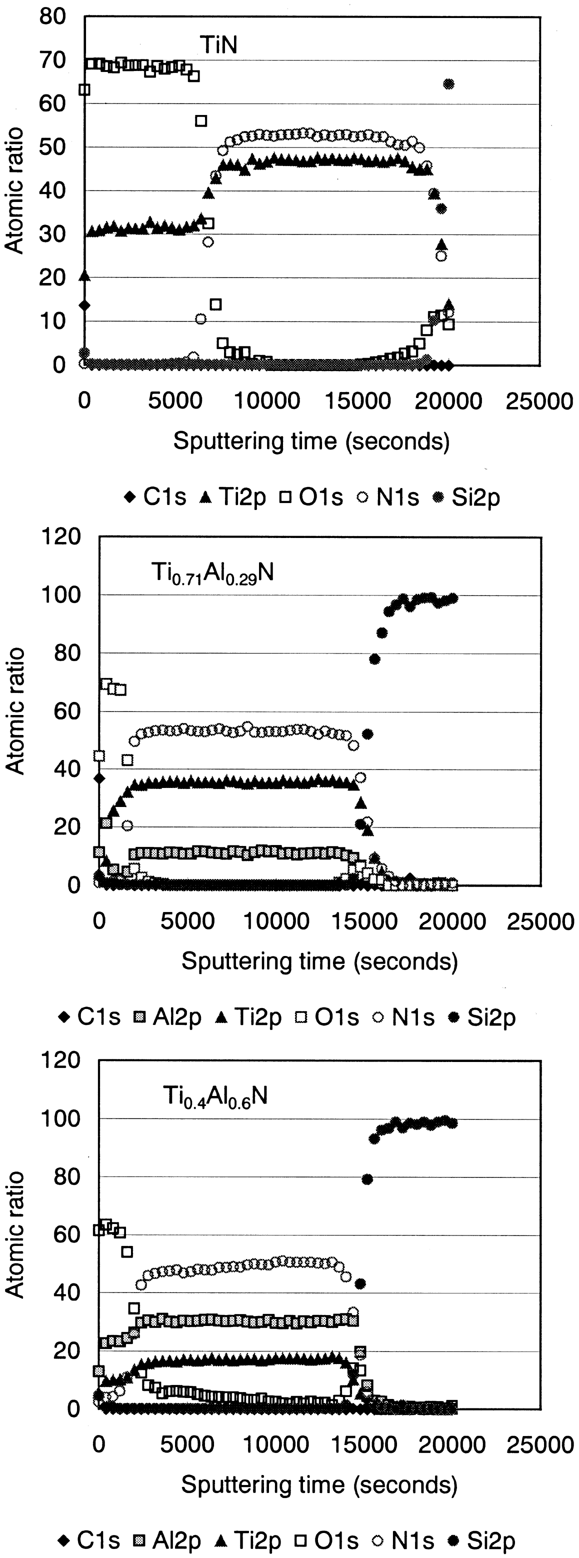

Fig. 6. XPS depth profiles of $Al_{1-x}Ti_xN$ (x= 0.40, 0.71 and 1.0) thin films on Si substrates. These films were annealed at 700°C for 10 min in pure oxygen.

some amount of the Al substitution is necessary to form effective aluminum-rich oxide layers to yield the oxidation resistance performance under the given annealing condition.

4. Conclusion

Optical, electrical, and oxidation resistance properties of the $Al_{1-x}Ti_xN$ ($0 \leqslant x \leqslant 1.0$) solid solution thin films were investigated. To our knowledge, this is the first report to investigate lattice vibration spectra in the IR region and photoelectron spectra of the $Al_{1-x}Ti_xN$ thin films. The frequency of the optical phonons at the center of the Brilloin zone in AlN decreased with increase of Ti content in the wurtzite AlN structure. Charge transfers from Al and N to Ti occured when the crystal structure changed from a wurtzite to an NaCl structure. XPS depth profiles showed that the aluminum substitution into TiN effectively improves the oxidation resistance, and the formation of an aluminum-rich oxide layer near the surface induced by oxygen annealing. For the practical application of aluminum-substituted TiN films as an electrically conductive barrier layer in memory devices, the appropriate amount of aluminum substitution should be determined under the given annealing conditions.

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