

Epitaxial Growth of $Ti_{1-x}Al_xN$ Buffer Layer on Si by Pulsed-Laser Deposition

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Thin films of $Ti_{1-x}Al_xN$ ($x=0$ to 0.4) were grown on Si (001) substrates by pulsed-laser deposition. The epitaxial relationship between the $Ti_{1-x}Al_xN$ film and the Si (001) substrate was confirmed by the X-ray pole figure and selected area electron diffraction patterns, and the crystallinity was evaluated from the full width at half maximum (FWHM) of the X-ray ω -rocking curve. It was found that the crystallinity of $Ti_{1-x}Al_xN$ deteriorated with increasing Al content (x). By depositing a TiN seed layer between Si (001) and $Ti_{1-x}Al_xN$, the crystallinity of $Ti_{1-x}Al_xN$ films was improved.

Key words: $Ti_{1-x}Al_xN$ thin film, epitaxial growth, buffer layer, pulsed-laser deposition

1. INTRODUCTION

The epitaxial ferroelectric oxides on Si have been paid much attention because of their promising device applications. However, epitaxial ferroelectric oxides can not be formed on Si substrate directly because large lattice mismatch and interdiffusion exist between the oxides (for instance, $Pb(Zr,Ti)O_3$) and Si. In order to form ferroelectric oxide on Si epitaxially, at least one kind of buffer layer is needed between the oxide and the Si substrate. The buffer layer is required to act as an epitaxy medium layer as well as a diffusion barrier layer. Some kinds of oxides as a buffer layer for growing perovskite materials on Si, such as CeO_2 ,¹⁾ yttria-stabilized zirconia (YSZ),²⁾ and MgO ³⁾ have been reported. For applications such as capacitor devices, however, these insulators can not be used as electrode materials. As a contact metallurgy in advanced microelectronic devices, titanium nitride (TiN) or $Ti_{1-x}Al_xN$ (TAN) thin film has been extensively studied because of their excellent property as a diffusion barrier, low electrical resistivity, and high thermal stability.^{4,5,6,7)} Several kinds of techniques to grow TiN or TAN thin films have been used, such as chemical vapor

deposition (CVD),⁸⁾ ion plating,⁹⁾ reactive sputtering,¹⁰⁾ reactive ion beam deposition,¹¹⁾ as well as pulsed-laser deposition (PLD).^{12,13)} Among these techniques, PLD is considered a powerful method for growing high-quality thin films because it can accurately control film composition.

In the present paper, we report the epitaxial growth of $Ti_{1-x}Al_xN$ on Si (001) by PLD. The crystallinity and resistivity of $Ti_{1-x}Al_xN$ films with different Al content ($x=0.1\sim 0.4$) were investigated. Furthermore, a way to improve the crystallinity of $Ti_{1-x}Al_xN$ films by forming a TiN seed layer on Si (001) prior to growing the $Ti_{1-x}Al_xN$ films is demonstrated.

2. EXPERIMENTAL

$Ti_{1-x}Al_xN$ thin films were grown on a Si (001) substrate by PLD with a pulsed ArF excimer laser (wavelength 193 nm). A Si (001) wafer (1x1-inch square) was cleaned for 2 minutes in a mixed solution of HF:distilled water:ethanol in a ratio of 1:1:10. Then, the wafer was mounted on a rotating holder heated at 740°C. The hot pressed $Ti_{1-x}Al_xN$ (density > 95%) targets with Al

contents of 0, 0.1, 0.2, 0.3, and 0.4 were ablated at a laser fluence of 4 to 5 J/cm² (repetition rate of 10 Hz) for growing $Ti_{1-x}Al_xN$ films at a base pressure of 3×10^{-8} Torr. The distance between the substrate and the target was fixed at 40 mm in order to get a deposition ratio of 2.5 to 3.0 nm/min.

The overgrowth process of films was monitored by *in situ* reflection high energy electron diffraction (RHEED) at an electron acceleration voltage of 25 kV. The structure of films and the epitaxial relationship between the $Ti_{1-x}Al_xN$ film and the Si (001) substrate were characterized by X-ray diffraction (θ - 2θ geometry), X-ray pole figure, and selected area electron-diffraction (SAD). The crystallinity was evaluated from the full width at half maximum (FWHM) of the X-ray ω -rocking curve. The microstructure of the interface between the film and the Si substrate was observed by transmission electron microscope (TEM). The surface and cross-section morphologies, and thickness of the films were evaluated by scanning electron microscopy (SEM) and atomic force microscopy (AFM).

3. RESULTS AND DISCUSSION

Figure 1 shows the θ - 2θ XRD pattern of the $Ti_{1-x}Al_xN$ ($X=0, 0.1, 0.2, 0.3, 0.4$) films grown on the Si (001) substrate. Though the intensity of peaks becomes weak with increasing Al content, it was confirmed that $Ti_{1-x}Al_xN$ films grow on Si (001) with [001] preferential orientation. To investigate the epitaxial relationship between $Ti_{1-x}Al_xN$ film and Si substrates as well as the interface of $Ti_{1-x}Al_xN/Si$, X-ray pole figure and cross-sectional TEM observations were taken. Figure 2 shows the typical X-ray pole figure taken for the (220) planes of a $Ti_{0.9}Al_{0.1}N$ film grown on Si (001) substrate. It indicates the $Ti_{0.9}Al_{0.1}N$ film grows on Si (001) with four-fold symmetry. Figure 3 shows the TEM image of the $Ti_{0.9}Al_{0.1}N/Si$ (001) interface with a [110] axis orientation. It was observed that the

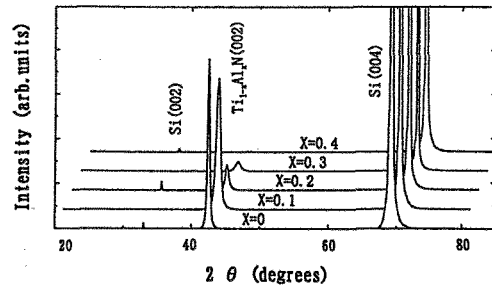


Fig. 1. XRD pattern of the $Ti_{1-x}Al_xN$ ($X=0, 0.1, 0.2, 0.3, 0.4$) films grown on Si (001) substrate.

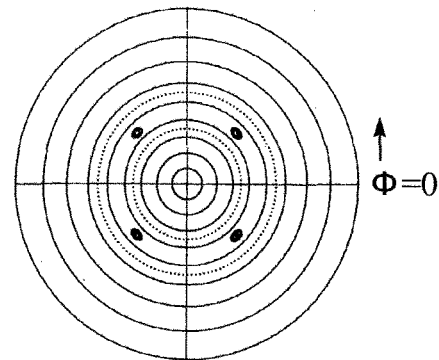


Fig. 2. X-ray pole figure of a $Ti_{0.9}Al_{0.1}N$ film grown on Si (001) substrate.

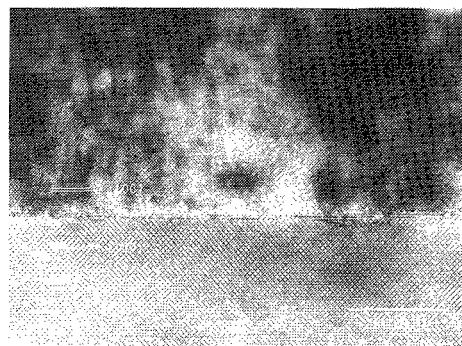


Fig. 3. Cross-sectional TEM image of the $Ti_{0.9}Al_{0.1}N/Si$ (001) interface.

lattice fringes of $Ti_{0.9}Al_{0.1}N$ {100} planes and Si {100} planes are parallel to each other. Above results show the epitaxial relationship between the $Ti_{1-x}Al_xN$ film and the Si (001) substrate was $Ti_{1-x}Al_xN$ (001) // Si

(001) and $Ti_{1-x}Al_xN$ [010] // Si [010]. Furthermore, as shown in Figure 3, though the dislocations originated from lattice mismatch exist in the interface, the interface between the $Ti_{0.9}Al_{0.1}N$ and the Si (001) substrate is smooth with no presence of interfacial oxide layer. The surface morphology of a $Ti_{0.9}Al_{0.1}N$ film was observed by AFM. A smooth surface was obtained with a roughness of $Ra = 0.512$ nm, which is considered to be enough to form smooth films on it.

Figure 4 shows the relationship between the electrical resistivity of the $Ti_{1-x}Al_xN$ films and Al content. The resistivity of the TiN film without Al substitution is $43.3 \mu\Omega \cdot cm$, which is same as reported by Lee,¹⁴⁾ though it is higher than that of TiN bulk ($21.7 \mu\Omega \cdot cm$). As Al content increases, the resistivity of $Ti_{1-x}Al_xN$ film increases exponentially up to $7.23 m\Omega \cdot cm$ (at $X=0.4$). This result indicates $Ti_{1-x}Al_xN$ films with low Al content are desirable as the electrode materials of devices using ferroelectric oxide films.

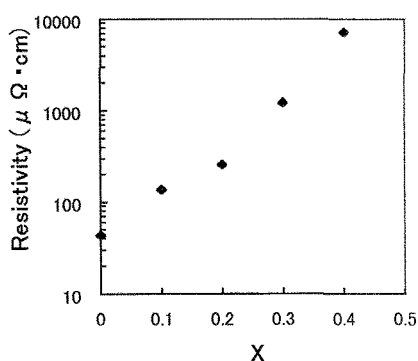


Fig. 4. Relationship between the electrical resistivity and Al content of the $Ti_{1-x}Al_xN$ films.

Yanase reported that the $Ti_{1-x}Al_xN$ film grows on a Si substrate epitaxially at an Al content up to 49%.¹⁰⁾ In the present study, it is confirmed that $Ti_{1-x}Al_xN$ film can be grown on Si(001) substrate epitaxially at Al content less than 40% ($X=0.4$) (no data available for Al contents more than 40%). However, since TiN and AlN show a different crystal structure and do not form a solid solution under an

equilibrium condition, the crystallinity of $Ti_{1-x}Al_xN$ film deteriorates as increasing Al substitution content (Fig. 1).

As a buffer layer, $Ti_{1-x}Al_xN$ film is required to be oxidation-resistant at high temperatures while oxide films such as $Pb(Zr,Ti)O_3$ form on it. If the $Ti_{1-x}Al_xN$ film is not oxidation-resistant enough, its surface structure will be destroyed during the formation of oxide films. A way to get more oxidation-resistant $Ti_{1-x}Al_xN$ film is to increase the Al substitution content in it.⁶⁾ However, above results show the crystallinity of $Ti_{1-x}Al_xN$ film deteriorates with increasing Al substitution content, and a good crystallinity of epitaxial oxide films on it is not expected. It is, therefore, necessary to find a way to grow a $Ti_{1-x}Al_xN$ buffer layer with not only oxidation-resistance but also good crystallinity.

Based on the evidence that TiN film without Al substitution grows epitaxially more easily than $Ti_{1-x}Al_xN$ film with Al substitution ($X>0$) on a Si (001) substrate, an attempt to improve the crystallinity of $Ti_{1-x}Al_xN$ film has been made by forming a TiN seed layer between the Si substrate and the $Ti_{1-x}Al_xN$ film. At first, the growth process of a TiN layer on a Si (001) substrate was observed by *in situ* RHEED with an incident beam parallel to the $\langle 100 \rangle$ of Si (001). And it was confirmed that a TiN structure was formed with a thickness below 10 nm. After growing the TiN seed layer (with approximate thickness of 10 nm), $Ti_{1-x}Al_xN$ film with a thickness of 250 nm was grown on the TiN seed layer. Figure 5 shows the RHEED patterns of the $Ti_{0.6}Al_{0.4}N$ film (250 nm) on the Si (001) directly and on the TiN/Si (001) (with a TiN seed layer on Si (001) surface). It was observed that $Ti_{0.6}Al_{0.4}N$ does not grow well on Si (001) directly, however, with a TiN seed layer of 10 nm thick, a diffraction pattern of NaCl structure was obtained from the $Ti_{0.6}Al_{0.4}N$ film. The same tendency was also observed of the other $Ti_{1-x}Al_xN$ ($X=0.1, 0.2, 0.3$) films.

Figure 6 shows the relationship between the FWHM

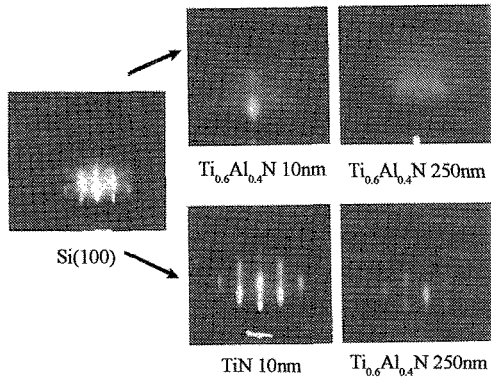


Fig. 5. RHEED patterns of the $Ti_{0.6}Al_{0.4}N$ film upper: on the Si (001) ; below: on the TiN/Si (001)

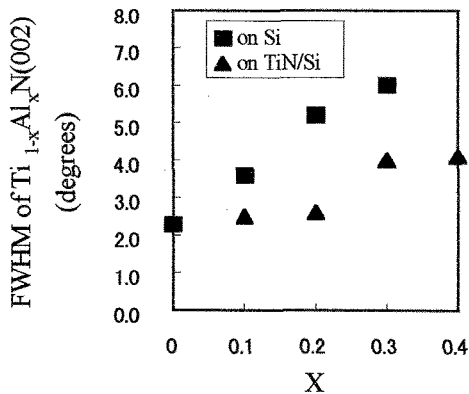


Fig. 6. Relationship between the FWHM and Al content of $Ti_{1-x}Al_xN$ films.

and Al content of $Ti_{1-x}Al_xN$ films (on the Si (001) and on TiN/Si (001)). It is shown that the FWHM value of the $Ti_{1-x}Al_xN$ film on either Si (001) or TiN/Si (001) increases with increasing Al content, indicating that the crystallinity of $Ti_{1-x}Al_xN$ film deteriorates with increasing Al substitution content. It is obvious that the crystallinity of $Ti_{1-x}Al_xN$ film grown on the TiN/Si (001) becomes better than that on Si (001) and that the crystallinity of $Ti_{1-x}Al_xN$ films with Al content less than 20% is improved to the same level as that of TiN film. On such a $Ti_{1-x}Al_xN$ buffer layer, it is promising to form epitaxial oxide ferroelectric films with excellent quality.

4. CONCLUSIONS

Thin films of $Ti_{1-x}Al_xN$ ($x=0$ to 0.4) were grown on Si (001) substrates at 740°C by pulse-laser deposition. The epitaxial relationship between the $Ti_{1-x}Al_xN$ film and the Si (001) substrate was confirmed as $Ti_{1-x}Al_xN$ (001) // Si (001) and $Ti_{1-x}Al_xN$ [010] // Si [010]. As Al substitution content increased, the crystallinity of the $Ti_{1-x}Al_xN$ film deteriorated and the resistivity increased exponentially. As an effective way to improve the crystallinity of $Ti_{1-x}Al_xN$ film, a TiN seed layer was formed on the Si (001) substrate prior to growing the $Ti_{1-x}Al_xN$ films. By growing the TiN seed layer on the Si (001) substrate, the crystallinity of $Ti_{1-x}Al_xN$ films with an Al content less than 20% was improved to the same level as that of TiN film.

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