Annealing Behaviours of Open Spaces in Thin Al_2O_3 Films Deposited on Semiconductors Studied Using Monoenergetic Positron Beams

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Open spaces in amorphous Al_2O_3 films fabricated by atomic layer deposition and in $AlON_x$ deposited by a reactive sputtering technique were probed by using monoenergetic positron beams. In these films, open spaces with three different sizes were found to coexist. The mean size and the concentration of open spaces were decreased by annealing at 800 °C in N_2 atmosphere, which was associated with rearrangements of the amorphous network in the films and their crystallization. Nitrogen incorporation into Al_2O_3 suppressed the shrinkage of network structures due to the annealing, which was attributed to the formation of a stable network through the introduction of Al–N bonding. For Al_2O_3 deposited on GaN, the temperature treatment above 800 °C led to the introduction of vacancy-type defects in the GaN substrate. This fact suggests that the change in the network structure of Al_2O_3 enhances chemical instability at the Al_2O_3/GaN interface and the out-diffusion of atoms from the substrate.

1. Introduction

Aluminium oxide (Al_2O_3) has been extensively studied for application as the gate insulators of metal–oxide–semiconductor field-effect transistors (MOSFET) because of its beneficial physical properties such as a large dielectric constant (9), large band gap (8.8 eV), and good adhesion [1]. It is also an ideal insulator for wide-gap semiconductors such as GaN due to an appropriate band offset at the insulator/semiconductor interface [2]. Al_2O_3 films can be fabricated on substrates by using several deposition techniques such as sputtering and atomic layer deposition (ALD) techniques [3–5]. It is well known that the deposition of gate oxides tends to introduce a high-density of carrier traps at the interface, and they are the major obstacles in device fabrication. Another concern with Al_2O_3 gate insulators is crystallization after annealing treatments because grain boundaries of crystalline Al_2O_3 act as a leakage path between semiconductors and electrodes [1]. It was reported that nitrogen incorporation into Al_2O_3 suppresses

its crystallization and hence improves the electrical properties of MOSFETs [5]. Although the benefits of nitridation are clear, only limited information is available regarding the effects of nitrogen incorporation on the matrix structure of amorphous Al_2O_3. Positron annihilation is an established technique for investigating vacancy-type defects and open spaces (pores) in crystalline and amorphous materials [6, 7]. Using this technique, insulators deposited on semiconductor substrates were successfully characterized [8–10]. In the present study, we used mono-energetic positron beams to study the annealing behaviours of open spaces in thin Al_2O_3 films fabricated by ALD and a reactive sputtering technique.

2. Experiment

25 nm thick Al_2O_3 films were deposited on GaN substrates at 300 °C by using the ALD method. Trimethylaluminium [TMA: $Al(CH_3)_3$] and H_2O were used as a precursor and oxidant gas, respectively. 10 nm thick $AlON_x$ ($x = 0\%$, 7%, and 25%) films were also deposited on SiO_2(8 nm)/Si templates at room temperature by using a reactive sputtering technique, where the sputtering target was Al, and N_2/O_2 and Ar/O_2 gas mixtures were used. The nitrogen content in the $AlON_x$ films was estimated by X-ray photoelectron spectroscopy. After the deposition, they were annealed at temperatures ranging

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up to 900 °C for 3–5 min in N_2 atmosphere. Details on the deposition conditions of the Al_2O_3 and $AlON_x$ films are given elsewhere [5, 11, 12].

In the present experiment, the Doppler broadening spectra of the annihilation radiation were measured with a Ge detector as a function of the incident positron energy E. The measured spectra were characterized by the S parameter, defined as the fraction of annihilation events in the energy range of 510.24–511.76 keV. The measured $S(E)$ profiles were analysed by VEPFIT, a computer program developed by van Veen et al. [13]. The lifetime spectrum of positrons implanted into the Al_2O_3 films was measured by using a pulsed monoenergetic positron beam at the NEPOMUC positron source of the Technische Universität München [14]. The spectra were analysed with a time resolution of about 200 ps (full-width at half-maximum: FWHM) by using the RESOLUTION computer program [15].

3. Results and discussion

Figure 1 shows the S values of $Al_2O_3(25$ nm$)$/GaN before and after annealing at 700, 800, and 900 °C. The S value decreased as E increased due to positron annihilation in the GaN substrate [16]. Using the relationship between the mean implantation depth of positrons and E [6], the incident positron energy corresponding to the thickness of the Al_2O_3 film was calculated as 2 keV. The observed increase in the S value at $E \cong 1$ keV, therefore, was associated with the annihilation of positrons in the Al_2O_3 film. For the samples annealed at 800 and 900 °C, the S value at $E \cong 1$ keV decreased, but humps appeared at $E = 2$–3 keV, which can be attributed to the introduction of vacancy-type defects near the Al_2O_3/GaN interface. The obtained S–E curves were analysed by using the VEPFIT code, and the solid curves in Fig. 1 were fitted to the experimental data.

Figure 2 shows the derived depth distributions of S obtained from the fittings. The region which corresponds to the Al_2O_3 film (0–25 nm) was divided into two blocks in order to obtain reasonable fitting results. It is well known that the GaO_x interlayer is introduced at the Al_2O_3/GaN interface [17]. Thus, the decrease in the S value near the interface could be due to the positron annihilation in such a layer. For the annealed samples, vacancy-type defects were found to be introduced up to a depth of 40–50 nm from the Al_2O_3/GaN interface. The introduction of such vacancies can be attributed to the atomic diffusion from the GaN substrate into the Al_2O_3 film during the annealing treatment.

Figure 3 shows (a) the annealing behaviour of the average of the S values measured at $E = 0.7$–0.9 keV for Al_2O_3/GaN and (b) those measured at $E = 0.4$–0.5 keV for $AlON_x$/SiO_2/Si ($x = 0$, 7, and 25%). These S values correspond to the annihilation of positrons in the Al_2O_3 or $AlON_x$ films, respectively. The S–E curve for $AlON_x$/SiO_2/Si was reported in Ref. [12]. The annealing behaviours of S shown in Fig. 3 were not influenced
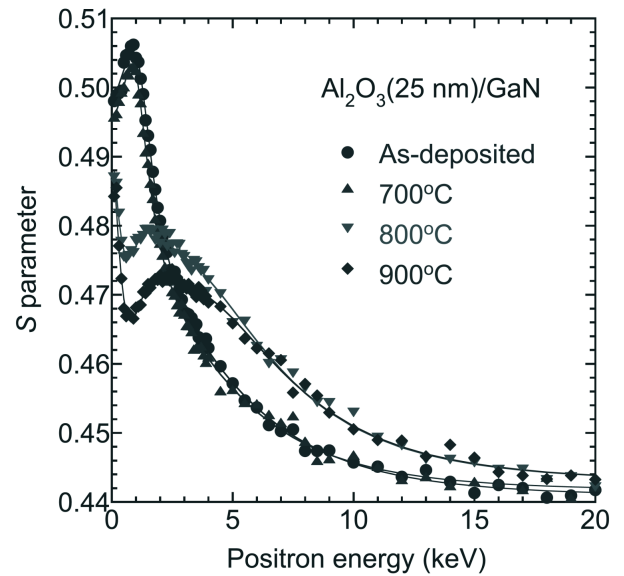

Fig. 1. S parameter as function of incident positron energy E for $Al_2O_3(25$ nm$)$/GaN before and after annealing treatments (700 °C, 800 °C, and 900 °C). Solid curves are fits to experimental data, and depth distributions of S are shown in Fig. 2.
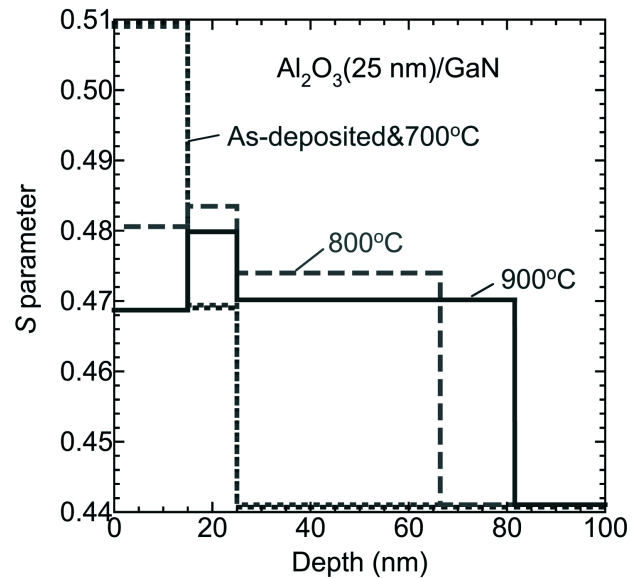

Fig. 2. Depth distributions of S parameter for Al_2O_3/GaN before and after annealing treatments.

by the substrates because these S values correspond to the top films of the samples. For Al_2O_3 and $AlON_x$ ($x = 0\%$), the S values decreased after annealing at 800 °C, suggesting a decrease in the mean size and/or concentration of open spaces. For $AlON_x$ with $x = 7\%$, however, the decrease in the S value above 800 °C was suppressed, but the effect of nitridation diminished for $AlON_x$ with $x = 25\%$.
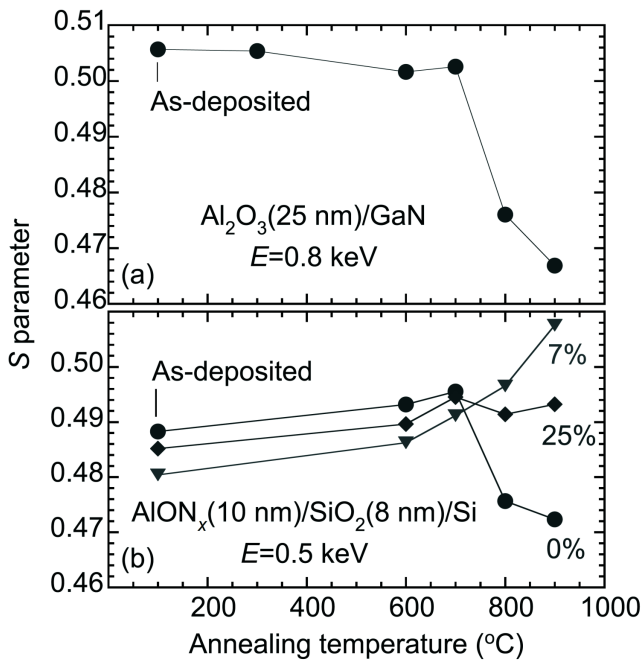
Fig. 3. (a) S parameter for Al$_2$O$_3$/GaN measured at $E = 0.8$ keV and (b) AlON$_x$/SiO$_2$/Si ($x = 0$, 7, and 25%) measured at $E = 0.5$ keV as function of annealing temperature.
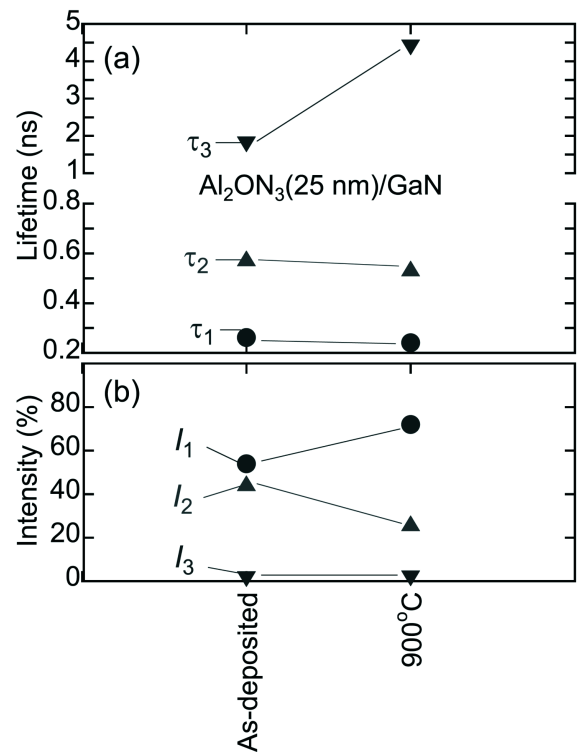

Fig. 4. (a) Positron lifetimes (τ_1, τ_2, and τ_3) and (b) their intensities (I_1, I_2, and I_3) measured at $E = 1$ keV for Al$_2$O$_3$/GaN before and after annealing at 900 °C.

For Al$_2$O$_3$/GaN before and after annealing at 900 °C, the lifetime spectra of positrons were measured at $E = 1$ keV, which corresponds to the annihilation of positrons in the Al$_2$O$_3$ film. The lifetime spectra were decomposed into three components, and the obtained lifetimes with corresponding intensities are shown in Fig. 4. Standard deviations of these parameters are smaller than the size of the symbols used in the figure. The third lifetime (τ_3) is typical for the annihilation of positronium (Ps: a hydrogen-like bound state between a positron and an electron) trapped by open spaces [7]. According to the relationship between the o-Ps lifetime and the size of the free volume used for amorphous polymers, the diameter of the open spaces (which are assumed to be spherical) in the as-deposited and annealed samples can be estimated to be 0.6 and 0.9 nm, respectively. The lifetime of positrons annihilated from the free state in crystalline α-Al$_2$O$_3$ was 0.143 ns [18]. Because the first and second positron lifetimes (τ_1 and τ_2) were longer than this value (Fig. 4), they were associated with the annihilation of positrons trapped by the open spaces. After 900 °C annealing, the values of τ_1 and τ_2 decreased from 0.262 ns to 0.241 ns and from 0.580 ns to 0.539 ns, respectively. The I_2 value also decreased from 44.0% to 26.6%. The change in the values of these parameters suggests that the decrease in the sizes of open spaces and in the concentration of the medium-sized open spaces. The observed change in these parameters can be attributed to the shrinkage of the network structure of Al$_2$O$_3$ due to crystallization.

Figure 5 shows the lifetimes and corresponding intensities for AlON$_x$ ($x = 0$, 7, and 25%) before and after annealing at 900 °C, where the lifetime spectra of positrons were measured at $E = 0.5$ keV. The τ_2 value increased as x increased, suggesting that the nitrogen incorporation increased the size of the medium-sized open spaces in the amorphous network. For the AlON$_x$ films with $x = 7\%$, the I_2 values increased after annealing, and the intensity of the short-lived component (I_1) decreased. This behaviour is consistent with the observed increase in the S value after annealing for AlON$_x$ with $x = 7\%$ (Fig. 3). For AlON$_x$ ($x = 0\%$), however, the change in the intensities was small, and the values of τ_1 and τ_3 decreased after annealing. These facts suggest that the nitrogen incorporation suppressed the shrinkage of open spaces after annealing. For the as-deposited AlON$_x$ with $x = 7$ and 25%, the I_2 values were smaller than that for AlON$_x$ with $x = 0\%$, suggesting that annealing treatment done at the appropriate temperature is indispensable for nitrogen incorporation to affect the network structure of the films.

Using the positron annihilation technique and X-ray photoelectron spectroscopy (XPS), Uedono et al. [10] reported the effect of nitrogen incorporation in 5 nm thick HfSiON$_x$ films deposited on Si substrates. They reported that the average size of open spaces increased as x increased, and this is mainly due to the increase in the density of Si–N bonds. In the present experiment, the
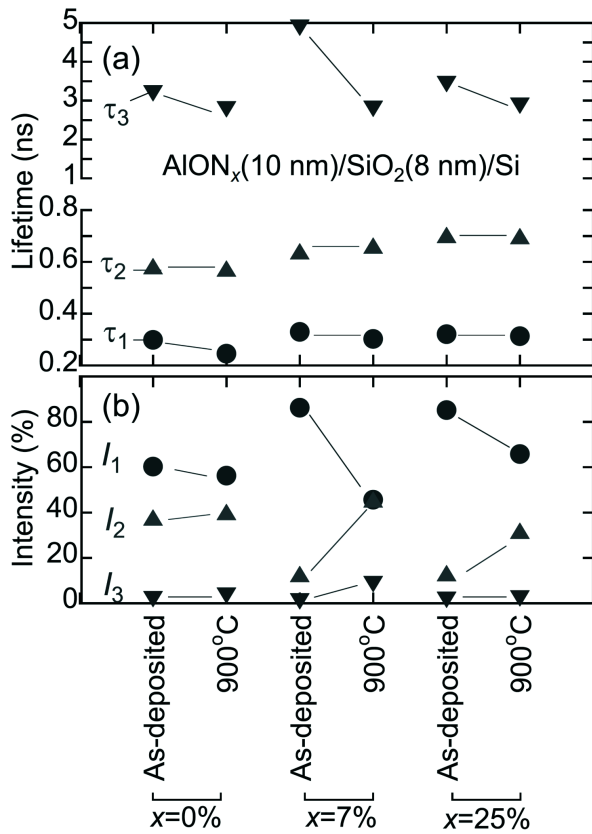
Fig. 5. (a) Positron lifetimes and (b) their intensities measured at $E = 0.5$ keV for $AlON_x/SiO_2/Si$ ($x = 0$, 7, and 25%) before and after annealing at $900\,°C$.

formation of Al–N bonds was also likely to increase the τ_2 value (the medium-sized open spaces). The nitrogen incorporation and resultant increase in the size of open spaces is thought to be related to the stabilization of the amorphous structure, which suppresses the crystallization of the film.

4. Summary

We studied the annealing behaviours of open spaces in Al_2O_3 films fabricated by ALD and in $AlON_x$ films deposited by reactive sputtering. Open spaces with three different sizes were detected in these films, and the mean size and concentration of open spaces decreased after $800\,°C$ annealing, suggesting the shrinkage of the network structure in the films and their crystallization. For $AlON_x$, the size of medium-sized open spaces was increased by nitrogen incorporation, and the shrinkage of the amorphous network was suppressed. For Al_2O_3 deposited on GaN, after annealing at $800\,°C$, vacancy-type defects were introduced into the GaN substrate because of the out-diffusion of atoms from GaN into the Al_2O_3 film. The present work suggests that positron annihilation parameters are sensitive to open spaces in thin Al_2O_3 and $AlON_x$ films, and it can provide useful information for process optimization for devices with the insulators.

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