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Positron Studies of Oxide-Semiconductor Structures


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The annihilation characteristics of positrons in SiO₂ films grown on Si substrates were studied by using monoenergetic positron beams. Doppler broadening profiles of the annihilation radiation and lifetime spectra of positrons were measured as a function of incident positron energy for SiO₂/Si structures fabricated by various oxidation techniques. From the measurements, it was found that the formation probability of positronium (Ps) atoms in SiO₂ films strongly depends on the growth condition of SiO₂ films. The present investigation shows that positrons provide a sensitive and nondestructive probe for the characterization of SiO₂ films grown on Si substrates.

1. INTRODUCTION

Oxide films used in LSI devices must exhibit good electrical characteristics and provide long-term reliability. Various charges and traps, however, are formed in SiO₂ films [1]. These defects affect ideal operations of LSI devices. The trapping sites of the carriers seem to be related to structures of SiO₂ films and of SiO₂/Si interfaces. Analyzing techniques such as electron spin resonance, X-ray photoelectron spectroscopy and electrical measurements are not adequate for full understanding of characteristics of SiO₂/Si interfaces and the atomic structure of SiO₂ films. With the development of high current monoenergetic positron beams, it is now possible to profile defects, multilayers and interfaces in the subsurface region [2]. The advantage of this technique is that the implantation profile of positrons can be adjusted to a restricted region of interest in the specimen by accelerating positrons to the desired energy. This technique has been successfully used to characterize Si₃N₄ films grown on Si substrates and SiO₂/Si interfaces [3-16]. In the present paper, we summarize studies of the annihilation characteristics of positrons in SiO₂ films grown on Si substrates by different oxidation techniques.

When positrons are implanted into condensed matter, they rapidly slow down to thermal energy. After this thermalization process, a positron annihilates with an electron from the surrounding medium into two 511 keV γ quanta. The motion of a positron-electron pair causes a Doppler shift in the energy of the annihilation photons. In a solid containing defects, a freely diffusing positron can be localized in vacancy-type defects by a Coulomb repulsion from ion cores. Since the momentum distribution of electrons in such defects is different from that in the bulk, one can detect defects by measurements of Doppler broadening profiles of the annihilation radiation. The change in the Doppler broadening spectrum is characterized by the lineshape parameter S, which is the ratio of counts in the central region of the spectrum to the total count [2]. When positrons are trapped by vacancy-type defects, the lifetime of positrons increases because of a reduced electron density in such defects. Thus, one can also detect vacancy-type defects by measurements of lifetime spectra of positrons.

A positronium (Ps) atom, a hydrogen-like bound state between a positron and an electron, is known to form in a vitreous quartz (v-SiO₂) [17]. Ps exhibits two spin states which are called para-Ps, p-Ps, and ortho-Ps, o-Ps, for the singlet state and the triplet state, respectively [18]. A ratio of the formation probability of o-Ps to that of p-Ps is 3 in vacuum due to spin statistics. The intrinsic lifetime of p-Ps is...
~125 ps and that of o-Ps is ~140 ns. In condensed matter, however, the lifetime of o-Ps is only 1~3 ns because the positron involved in o-Ps can annihilate with one of the surrounding electrons rather than its own partner. This process is called the "pick-off" annihilation of o-Ps.

2. EXPERIMENT

The specimens used in the present experiment were Czochralski-grown Si wafers with a (100) orientation (p-type, 10\(\Omega\)cm). The oxide films with a thickness of 166 nm were grown on the Si substrates in \(O_2/\text{H}_2\) gas at 650 °C and at 1000 °C, respectively. In order to know the annihilation characteristics of positrons at the \(\text{SiO}_2/\text{Si}\) interface, positrons implanted into the \(\text{SiO}_2\) film were accumulated at the \(\text{SiO}_2/\text{Si}\) interface by applying a gate voltage to the metal/oxide/semiconductor (MOS) structure. In order to form the MOS structure, the oxide film with a thickness of 400 nm was grown on the Si substrate in \(O_2/\text{H}_2\)-gas at 1000 °C. Then, polycrystalline (poly-) Si with a thickness of 100 nm was prepared by a chemical vapor deposition at 640 °C and phosphorus atoms were diffused into the poly-Si film at 875 °C in order to form a metallic electrode. During the measurements, the Si substrate was grounded and a gate voltage, \(V_g\), was applied to the poly-Si film.

The annihilation characteristics of positrons in \(\text{SiO}_2\) films grown by an atmospheric-pressure chemical vapor deposition (APCVD) using tetraethylorthosilicate (TEOS, \(\text{Si(OC}_2\text{H}_5)_4\)) and \(O_3\) were studied. The deposition apparatus of APCVD was described elsewhere [19]. The APCVD-SiO\(_2\) films were prepared at different substrate temperatures and at different \(O_3\) concentrations. The \(\text{SiO}_2\) film grown by CVD using SiH\(_4/\text{N}_2\)O and that by wet oxidation were also studied. The growth conditions of those films are listed in Table I. The contents of \(H_2O\) and bonding structures in the APCVD-SiO\(_2\) films were analyzed by a moisture evolution analyzer and Fourier transform infrared spectroscopy (FTIR), respectively.

It is well known that impurities such as \(H_2O\) or \(-\text{OH}\) bonds with high concentration exist in CVD-SiO\(_2\) films grown by using TEOS/\(O_3\) [20]. The implantation of oxygen ions into Si substrates decreases the concentration of such impurities in SiO\(_2\) films. Separation by implanted oxygen (SIMOX) wafers were characterized in the present experiment. The implantation of 200 keV O\(^+\) ions was performed at 550 °C up to the dose of 1x10\(^{18}\) O/cm\(^2\). After ion implantation, the specimen was subsequently annealed at 1325 °C under Ar and \(O_2\) gas atmosphere for 8 hours. After this annealing treatment, the implantation was performed again with the same conditions. Finally the specimen was
annealed again. Thus, the total implantation dosage was $2 \times 10^{18}$ O/cm$^2$. The conditions of the specimens after each annealing treatment are listed in Table II, where the thickness of the silicon on insulator (SOI) layer and that of the SiO$_2$ layer were measured using a cross-sectional transmission electron microscope.

The monoenergetic positron beam line at the University of Tsukuba was used for measurements of Doppler broadening profiles [21]. Positrons emitted from a $^{22}$Na source were moderated by well-annealed tungsten foils. The slow positrons obtained were guided by a magnetic field through multiple discrete acceleration lenses and struck the specimen with an adjusted energy between 0 keV and 30 keV. Doppler broadening profiles of the annihilation radiation were measured with a Ge detector as a function of incident positron energy, $E$. The annihilation spectrum was characterized by the $S$ parameter.

The observed $S$-$E$ relations for the SiO$_2$/Si specimens were analyzed by a computer code "VEPFIT" developed by van Veen et al. [22]. The one-dimensional diffusion model of positrons is described by [21]:

$$D_+ \frac{d^2 n(z)}{dz^2} - \frac{d}{dz} \{v(z)n(z)\} - \kappa_{\text{eff}}(z)n(z) + P(z,E) = 0,$$

where $D_+$ is the diffusion coefficient of positrons, $n(z)$ is the probability density of positrons at a distance $z$ from the surface, $v(z)$ is the drift velocity, $\kappa_{\text{eff}}(z)$ is the effective decay rate of positrons, and $P(z,E)$ is the implantation profile of positrons. $v(z)$ is connected to the mobility of positrons, $\mu$, and the electric field, $E(z)$ by the relation: $v(z) = \mu E(z)$. In VEPFIT, $P(z,E)$ is described by the expression:

$$P(z,E) = m \frac{m-1}{z_0^m} \exp\left(-\frac{z}{z_0}\right)^m,$$

where $m$ is the shape parameter of $P(z,E)$. $z_0$ is proportional to the mean implantation depth of positrons, $\bar{z}$, as follows: $z_0 = \bar{z}/\Gamma(1/m)+1$, where $\Gamma$ is the gamma function. $\bar{z}$ has a power-law dependence on the incident positron energy, $\bar{z} = A E^n$, where $A$ is a constant depending on the density of the target, $\rho$, ($A = C/\rho$, $C$ is a constant) and $n$ is an energy- and material-dependent constant. In this article, the values of $m$, $n$ and $C$ were fixed as 2, 1.6 and 3.32 $\mu$g/cm$^2$keV$^{-1.6}$ [11], respectively. The observed $S$-$E$ plots for the SiO$_2$/Si specimens were fitted by the relation,

$$S(E) = S_S F_S(E) + S_0 F_0(E) + S_1 F_1(E) + S_{S1} F_{S1}(E),$$

where $S_S$, $S_0$, $S_1$ and $S_{S1}$ are the characteristic values of the $S$ parameter for the annihilation of positrons at the surface, in the SiO$_2$ film, at the SiO$_2$/Si interface and in the Si substrate, respectively. $F(E)$ is the fraction of positrons annihilating in each region ($XF_i(E) = 1$).

A pulsed monoenergetic positron beam line constructed at Electrotechnical Laboratory was used in order to measure lifetime spectra of positrons. The detail of the system was described elsewhere [23]. The lifetime spectra were obtained by measuring the time interval between the timing signal derived electrically from the pulsing system and the annihilation $\gamma$ ray detected by a BaF$_2$ scintillation detector. Total counts of about $2 \times 10^5$ were accumulated for each lifetime spectrum.

The lifetime spectrum of positrons, $I(t)$, is expressed by,

$$I(t) = \sum I_i \exp(-t/T_i),$$

where $T_i$ and $I_i$ are the lifetime of the $i$-th component and its intensity ($\Sigma I_i = 1$), respectively. The observed lifetime spectra in the present experiment were analyzed by RESOLUTION [24] with the time resolution of $\sim 280$ ps.

3. RESULTS AND DISCUSSION

Figure 1 shows the $S$ parameter as a function of incident positron energy, $E$, for the SiO$_2$(166 nm)/Si specimens fabricated by thermal oxidation. The mean implantation depth of positrons is shown below the horizontal axis in the figure, together with $E$. At high $E$ (20 keV), the value of the $S$ parameter was
found to approach a constant value. This indicates that almost all positrons are implanted into bulk Si in this energy range. At $E=4$ keV, dips in the $S$-$E$ plots were observed. Since this energy corresponds to the depth of the $SiO_2$/Si interface, the observed decrease in the value of $S$ can be associated with the annihilation of positrons at the $SiO_2$/Si interface. In the region between 2 keV and 3 keV, the value of $S$ was larger than that at $E=4$ keV. This is due to the annihilation of positrons in the $SiO_2$ film. For the $SiO_2$/Si specimen fabricated at 1000 °C, the value of $S$ in this energy range was found to be larger than that for the specimen fabricated at 650 °C. At $E=0$ keV, the lowest value of $S$ was observed. This is associated with the annihilation of positrons at the surface of the specimen.

The observed $S$-$E$ plots were analyzed by VEPFIT. The diffusion length of positrons in electric-field-free Si, $L_d$(Si), and the value of $S_S$ were fixed at 200 nm [25] and 0.5343, respectively. According to the analysis of $S$-$E$ plots for $SiO_2$/Si specimens by An et al. [12], the thickness of the interface layer and the diffusion length of positrons in this layer were fixed at 2 nm and 0.01 nm, respectively. It was found that both $S$-$E$ plots can be fitted by using $S_1=0.49$ and $E_S=5 \times 10^3$ V/cm, where $E_S$ is the electric field in the Si substrate. The value of $E_S$ was found to strongly depend on the shape parameters of the implantation profile of positrons and the value of $S_1$. The results of the fitting are shown as solid curves in Fig. 1.

The derived values of $S_0$ were 0.524 and 0.526, and those of the diffusion length of positrons in the $SiO_2$ film, $L_d$(Si), were 9.7 nm and 8.9 nm, for the specimens fabricated at 650 °C and at 1000 °C, respectively. Nielsen et al. [4] already reported that the value of the $S$ parameter drastically decreased at the $SiO_2$/Si interface. Lynn et al. [6] found that the annihilation characteristics of positrons at the $SiO_2$/Si interface were very sensitive to hydrogen exposure. They suggested that the decrease of $S$ at the $SiO_2$/Si interface can be attributed to the strong interaction between positrons and the hydrogen modified interface. The small value of $S_1$ (0.49) derived in the present experiment also can be attributed to such phenomena.

Figures 2 and 3 show the lifetimes and the second intensity for the $SiO_2$ (166 nm)/Si specimens as a function of incident positron energy, where the observed lifetime spectra were decomposed into two components. In Fig. 2, the value of $t_2$ was found to be shorter than the intrinsic lifetime of o-Ps (~140 ns). However, this value is longer than the typical lifetime of positrons in crystalline solids [17]. Therefore, this annihilation mode can be associated with the pick-off annihilation of o-Ps. The presence of o-Ps should be associated with that of p-Ps, too. Thus, the formation probability of Ps in the $SiO_2$ films can be estimated as about 90% ($I_3+I_3/3$). Dannefaer et al. [26] reported that the lifetime spectrum for a single crystal quartz ($\alpha$-$SiO_2$) can be decomposed into three components. They reported that the longest lifetime was 1.4 ns with the intensity of 1.5%. This component can be associated with the pick-off annihilation of o-Ps.

For the $SiO_2$ films, the intensity corresponding to the annihilation of Ps was about 90%, while that in $\alpha$-$SiO_2$ (~2%) is far less than this value. Because of the high sensitivity of positrons for vacancy-type defects, almost all positrons are considered to be trapped by open atomic spaces in amorphous materials. If a specimen contains a large number of open-spaces such as microvoids or pores, positrons can form Ps in such regions under some conditions. Amorphous $SiO_2$ specimens have been considered to contain such open-space defects. Uedono and Tanigawa [27] investigated the annihilation characteristics of Ps in $\nu$-$SiO_2$ specimens by measurements of two-dimensional angular correlation annihilation radiation. From the measurements, it was found that Ps formed in the $\nu$-$SiO_2$ specimens annihilates with broadened momentum distribution. This fact was attributed to the
momentum uncertainty due to the localization of Ps in a finite dimension of open-space defects. Therefore, it can be concluded that almost all Ps formed in amorphous SiO2 specimens is trapped by open-space defects. For the SiO2/Si specimen fabricated at 650 °C, the value of $\tau_2$ at $E=2$ keV was found to be smaller than that for the specimen at 1000 °C (Fig. 2). This result suggests that the mean size of open-space defects in the SiO2 film grown with low substrate temperature is smaller than that in the SiO2 film grown with high substrate temperature. Therefore, it can be concluded that the size of open-space defects decreases with decreasing the growth rate of the SiO2 film. The slow growth rate is considered to cause a dense network in the SiO2 film.

In order to know the annihilation characteristics of positrons at the SiO2/Si interface in more detail, the positron lifetime spectra were measured as a function of the gate voltage for the MOS specimen. The observed lifetime spectra were decomposed into two components. Figures 4 and 5 show the gate voltage dependence of the lifetime and that of the second intensity at $E=5.5$ keV. At this incident positron energy, $I_2$ coincides with the region of the SiO2 film. From Figs. 4 and 5, it was found that the value of $I_2$ decreased with increasing gate voltage, although no drastic change in the value of $\tau_2$ was observed. In the inversion state of the MOS specimen, positrons implanted into the SiO2 film diffuse towards the SiO2/Si interface by the electric field. Thus, the observed decrease in the value of $I_2$ can be attributed to the enhanced diffusion of positrons towards the SiO2/Si interface. This decrease of $I_2$ can be attributed to an accumulation of positrons at the SiO2/Si interface and the resultant inhibition of the Ps formation. Since the annihilation from the p-Ps state produces $\gamma$ rays with very sharp energy width, the annihilation of p-Ps increases the value of the $S$ parameter. Therefore, the observed decrease in the value of $S$ parameter at the SiO2/Si interface (Fig. 1) can be attributed to the inhibition of the Ps formation.

Figures 6 and 7 show the lifetimes of positrons and the second intensities for the SiO2 films fabricated by CVD and by wet oxidation, respectively. From Fig. 7, it can be seen that the value of $I_2$ for the APCVD-SiO2 films grown by using TEOS/O3 was smaller than that for the thermal oxide film. This means that the formation probability of Ps decreased in the APCVD-SiO2 specimens. It can be concluded that the formation probability of Ps increased with increasing the substrate temperature and it decreased with decreasing the concentration of O3. From the measurements of FTIR, it was found that the concentration of -OH bonds decreased with increasing the substrate temperature. By using a moisture evolution analyzer, the content of H2O for the APCVD-SiO2 film grown at 0.5 %O3 was
Fig. 4 The gate voltage dependence of the lifetime at $E=5.5$ keV. The lifetime spectra were decomposed into two components, where the long-lived component was attributed to the pick-off annihilation of o-Ps.

Fig. 5 The gate voltage dependence of the intensity corresponding to the pick-off annihilation of o-Ps at $E=5.5$ keV.

Fig. 6 The lifetimes of positrons for the SiO$_2$ films fabricated by CVD and by wet oxidation.

Fig. 7 The second intensities for the SiO$_2$ films fabricated by CVD and by wet oxidation.

obtained as 4.3 wt% and that for the film grown at 5% O$_3$ was 2.2 wt%, where the substrate temperature was 400 °C. This fact suggests that the concentration of -OH bonds in the APCVD-SiO$_2$ film decreases with increasing the concentration of O$_3$. Since the formation of Ps needs larger open spaces or a lower electron density than the volume or electron density around point defects, the trapping of positrons by point defects such as oxygen vacancies is considered to suppress the formation of Ps. Uedono et al. [28] found that the formation probability of Ps in v-SiO$_2$ was decreased by the trapping of positrons into
vacancy-type defects introduced by electron irradiation. However, for the APCVD-SiO₂ films grown by using TEOS/O₃, the concentration of point defects is considered to be low, because of the high concentration of H₂O and a resultant formation of Si-OH bonds. Thus, the concentration of the point defects in the thermal oxide film or in the CVD-SiO₂ film grown by using SiH₄/N₂O is considered to be higher than that for the APCVD-SiO₂ films grown by using TEOS/O₃. Therefore, the inhibition of the Ps formation can be attributed to the interaction between positrons and -OH bonds in SiO₂ films. For the SiO₂ films with the high concentration of -OH bonds, positrons are considered to be trapped by -OH bonds and annihilate before the formation of Ps.

The inhibition of the Ps formation by the trapping of positrons into vacancy-type defects was observed for the SIMOX specimens [29]. Figures 8 and 9 show the lifetimes of positrons and the second intensities for the 200-keV O⁺-ion implanted Si specimens, respectively. In Fig. 9, it can be seen that the value of I₂ was increased by the first annealing treatment. Although the value of I₂ decreased after the second ion implantation, the highest value of I₂ was observed after the final annealing treatment. However, no drastic change in the value of τ₂ was observed for the specimens after each annealing treatment (Fig. 8). The changes in the value of I₂ are due to the formation of the SiO₂ layer upon annealing treatment. For the annealed specimen with a dose of 2x10¹⁸ O/cm², the highest value of I₂ was observed. However, the specimen with a dose of 2x10¹⁸ O/cm² before the annealing treatment, the value of I₂ was smaller than that for the annealed one. This fact can be attributed to the trapping of positrons by vacancy-type defects introduced by O⁺-ion implantation, and the resultant inhibition of the Ps formation. For the annealed specimen with a dose of 1x10¹⁸ O/cm², the value of I₂ was smaller than that for the one with a dose of 2x10¹⁸ O/cm². For the annealed specimen after the implantation of O⁺-ions with a dose of 1x10¹⁸ O/cm², because of a lack of oxygen atoms, oxygen vacancies with high concentration are considered to exist in the SiO₂ film. Thus, the observed small value of I₂ was also attributed to the inhibition of the Ps formation by the trapping of positrons by vacancy-type defects.

Fig. 8 The second lifetime τ₂ as a function of incident positron energy for the 200-keV O⁺-ion implanted specimens as-implanted and after annealing.

Fig. 9 The second component I₂ as a function of incident positron energy for the 200-keV O⁺-ion implanted specimens as-implanted and after annealing.

4. CONCLUSION

We have studied the annihilation characteristics of positrons in SiO₂/Si specimens fabricated by various oxidation techniques. In the SiO₂ film, about 90% of positrons were found to annihilate from the Ps states. This fact was due to the trapping of positrons by open-space defects and the resultant enhanced formation of Ps in such regions. For the SiO₂/Si specimen fabricated at 650 °C, the value of
The parameter $\tau_2$ at $E=2$ keV was found to be smaller than that for the specimen at 1000 °C. This result suggests that the mean size of open-space defects in the SiO$_2$ film grown with low substrate temperature is smaller than that in the SiO$_2$ film grown with high substrate temperature. In the CVD-SiO$_2$ films, the formation probability of Ps was found to be lower than that in the SiO$_2$ film grown by wet oxidation. The formation probability of Ps decreased with increasing the concentration of -OH bonds in the APCVD-SiO$_2$ films grown by using TEOS/O$_3$. These facts can be attributed to the interaction between positrons and -OH bonds. For the SIMOX specimens, the intensity of o-Ps was found to be sensitive to the formation of the SiO$_2$ layer upon the annealing treatment. The present investigation shows that positrons provide a sensitive and nondestructive probe for the characterization of SiO$_2$ films grown on Si substrates.

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