Advanced Materials '93, I / B: Magnetic, Fullerene, Dielectric, Ferroelectric,
Diamond and Related Materials, edited by M. Homma et al.
Trans. Mat. Res. Soc. Jpn., Volume 14B

© 1994 Elsevier Science B.V. All rights reserved.

Defects in SiO_2 films deposited on Si substrates probed by monoenergetic positron beams

A. Uedono[a], L. Wei[a], S. Tanigawa[a], R. Suzuki[b], H. Ohgaki[b], T. Mikado[b] and Y. Ohji[c]

[a]Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

[b]Electrotechnical Laboratory, Umezono, Tsukuba, Ibaraki 305, Japan

[c]Central Research Lab., Hitachi, Ltd., Kokubunji, Tokyo 185, Japan

The positron annihilation in a metal/oxide/semiconductor was 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 a polycrystalline Si(100 nm)/SiO_2(400 nm)/Si specimen. Applying a gate voltage between the polycrystalline Si film and the Si substrate, positrons implanted into the SiO_2 film were accumulated at the SiO_2/Si interface. From the measurements, it was found that the annihilation probability of ortho-positronium (ortho-Ps) drastically decreased at the SiO_2/Si interface. The observed inhibition of the Ps formation was attributed to an interaction between positrons and defects at the SiO_2/Si interface.

1. INTRODUCTION

The reliability and the stability of the most semiconductor devices are intimately related to their surface and interface conditions. Since they are directly related to the most planar devices and integrated circuits, the role of metal/oxide/semiconductor (MOS) structures is very important. Developments of large scale integrated (LSI) devices require a precise control of defects in oxide films and at oxide/semiconductor interfaces, because the defects were known to affect the performance of LSI devices.

The positron annihilation technique is now established as one of the best method for the investigation of defects in materials [1]. This technique enables us to detect defects such as monovacancies or vacancy-clusters with very high sensitivity. Monoenergetic positron beams were used to probe properties of surfaces, subsurface defects and buried interfaces [2-5]. The advantage of this technique is that the implantation depth of positrons can be adjusted in the region of interest by changing the incident positron energy. Thus, monoenergetic positrons can be used as a nondestructive depth-sensitive probe. In the present paper, we applied the monoenergetic positron beams for the study of defects in the MOS structure.

A positron implanted into the specimen eventually annihilates with an electron producing 511-keV γ rays. Since a positron is positively charged, it is repelled from ion cores by a Coulomb interaction. Thus, if a specimen contains vacancy-type defects, there is a finite probability of positrons being trapped in these regions. The lifetime of positrons in materials reflects the density of electrons in the places where the positron annihilates. Due to a reduced electron density in vacancy-type defects, the lifetime of positrons trapped by such defects increases. Thus, measurements of lifetime of positrons provide information of vacancy-type defects. The relationship between the lifetime of positrons and the species of defects is well established for metals and semiconductors [1,6].

The motion of the positron-electron pair causes a Doppler shift in the energy of the annihilation photons. Since the momentum distribution of electrons in defects is different from that in the bulk, one can also detect defects through measurements of Doppler broadening profiles of the annihilation radiation. The change in the Doppler broadening spectrum is characterized by the line shape parameter S, which is the ratio of counts in the central region of the spectrum to the total count [1].

A positronium (Ps) atom, a hydrogen-like bound state between a positron and an electron, may form in insulators [7]. Ps exhibits two spin states which are called "para-Ps" and "ortho-Ps" for the singlet state and the triplet state, respectively. A ratio of the formation probability of ortho-Ps to that of para-Ps is 3 in vacuum. The intrinsic lifetime of para-Ps is ~125 ps and that of ortho-Ps is ~140 ns. In condensed materials, however, the lifetime of ortho-Ps is only 1~5 ns because the positron involved in ortho-Ps can annihilate with one of surrounding electrons rather than its own partner. This process is called "pick-off" annihilation of ortho-Ps [7].

2. EXPERIMENTAL

The specimen used in the present experiment was a Czochralski-grown Si (Cz-Si) wafer with a (100) orientation (p-type, 10 Ωcm). The oxide film with a thickness of 400 nm was grown on the Si substrate in O_2/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. In order to accumulate positrons at the SiO_2/Si interface, a gate voltage, V_g, was applied to the poly-Si film.

The monoenergetic positron beam line installed at the University of Tsukuba was used for the present experiment [8]. Doppler broadening profiles of the annihilation radiation were measured by a Ge detector as a function of incident positron energy. The observed annihilation spectrum was characterized by the S parameter [1]. The pulsed monoenergetic positron beam line constructed at the Electrotechnical Laboratory was also used in order to measure lifetime spectra of positrons. The detail of the system was described elsewhere [9].

3. RESULTS AND DISCUSSION

Figure 1 shows the S parameter as a function of incident positron energy, E, for the poly-Si/SiO_2/Si specimen, where the mean implantation depth of positrons is also shown below the horizontal axis. From the Figure, it can be seen that the value of S was found to be nearly constant at high incident positron energy ($E \cong 30$ keV). This means that almost all positrons implanted with this energy range annihilate in the Si substrate. Therefore, the saturated value of S (0.5235) is the characteristic value of S for the positron annihilation in the Si substrate. In the region between 5 keV and 10 keV, a decrease in the value of S was found. This corresponds to the annihilation of positrons in the SiO_2 film. An increase in the value of S at $E \cong 2$ keV can be associated with the annihilation of positrons in the poly-Si film. Because of the high sensitivity of positrons for vacancy-type defects, almost all positrons are considered to be trapped by vacancy-type defects in the poly-Si film. It is generally accepted that the characteristic value of S for the

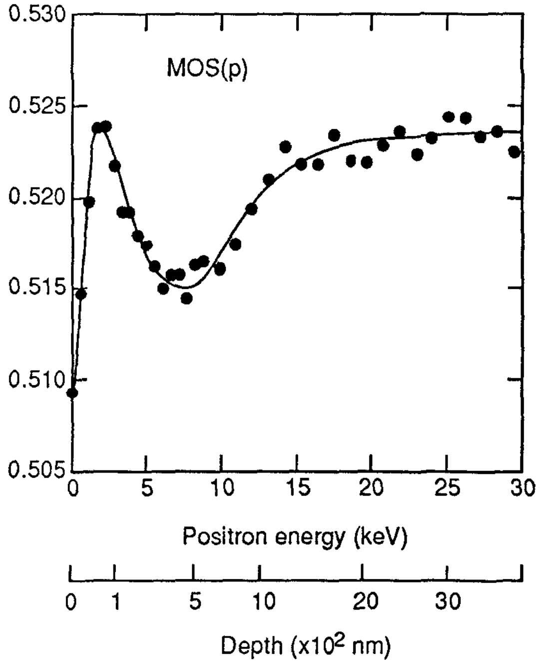

Figure 1. The line shape parameter S as a function of incident positron energy for the polycrystalline Si(100 nm)/SiO_2(400 nm)/Si specimen.

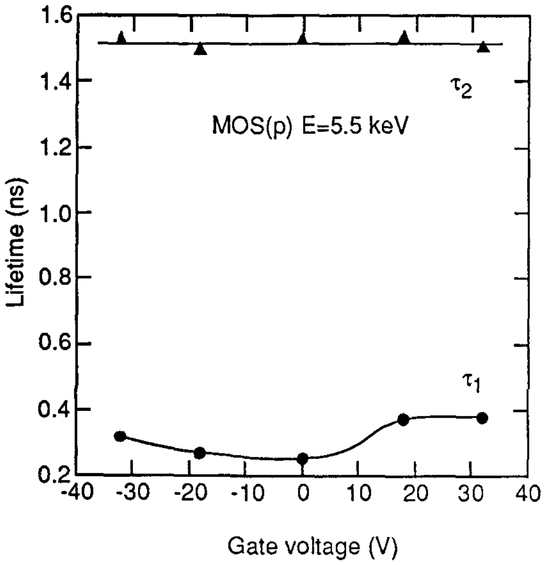

Figure 2. The gate voltage dependence of the lifetime at E=5.5 keV. The lifetime spectra were decomposed into two components, where the long-lived component was attributed to the pick-off annihilation of ortho-Ps.

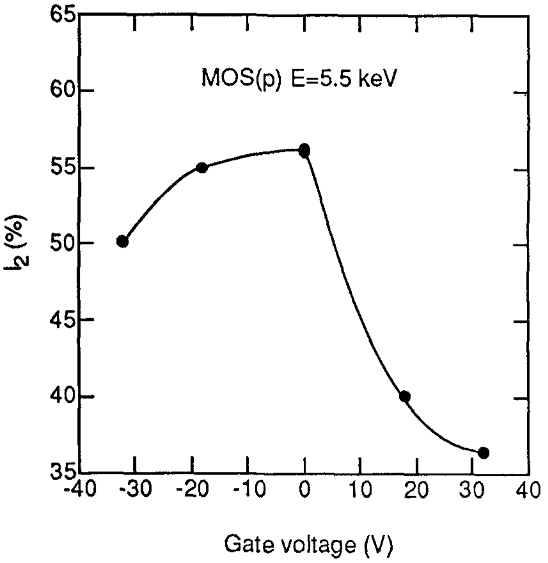

Figure 3. The gate voltage dependence of the intensity corresponding to the pick-off annihilation of ortho-Ps at E=5.5 keV.

annihilation of positrons trapped by vacancy-type defects is larger than that for the bulk. Thus, the observed increase in the value of S is attributed to the annihilation of positrons trapped by vacancy-type defects in the poly-Si film.

In order to know the annihilation characteristics of positrons in the SiO_2 film, the lifetime spectra were measured at E=5.5 keV. The observed spectra were decomposed into two components. Figures 2 and 3 show the lifetimes and their intensities as a function of the gate voltage, respectively. From Fig. 2, it can be seen that the value of τ_2 was almost constant. The average value of τ_2 was calculated as 1.5 ns. The values of τ_2 are longer than the typical lifetime of positrons in crystalline solids; for example, the lifetime of positrons in a bulk Si is 220 ps and that in vacancy-type defects in Si ranges between 270 ps and ~500 ps (ref. 6). Thus, the observed second component can be associated with the pick-off annihilation of ortho-Ps. In Fig. 3, the value of I_2 at V_g=0 V was 56 %. The formation probability of Ps in a crystalline quartz is far less than this value [10,11]. If a specimen contains open-space defects such as microvoids or pores, positrons can form Ps in such regions under some conditions. Amorphous SiO_2 have been considered to contain such open-space defects. Because of the high sensitivity of positrons for vacancy-type defects, positrons may be trapped by such region before the formation of Ps. Thus, the formation of Ps in the SiO_2 film is considered to be enhanced by the trapping of positrons in open-space defects. Since the lifetime of ortho-Ps and its formation probability depend on the size and the concentration of open-space defects [12], one can detect such defects in SiO_2 films by measurements of the lifetime spectra of positrons.

In Fig. 3, it can be seen that the value of I_2 decreased with increasing the gate voltage. In inversion sate of MOS capacitors, positrons implanted into the SiO_2 film diffuse towards the SiO_2/Si interface by the electric field. Thus, the observed decrease in the value of I_2 can be attributed to an accumulation of positrons at the SiO_2/Si interface and a resultant inhibition of the Ps formation. Leung *et al.* [5] reported a drastic decrease in the value of S at the SiO_2/Si interface.

They also reported that the annihilation characteristics of positrons at the SiO_2/Si interface were very sensitive to hydrogen exposure. This fact can be attributed to the strong interaction between positrons and the hydrogen modified interface. Since the annihilation from the para-Ps state produces γ rays with very sharp energy width, the annihilation of para-Ps increases the value of the S parameter. Therefore, the decrease in the value of S at the SiO_2/Si interface can be attributed to the inhibition of the Ps formation.

Klier *et al.* [13] reported an adsorption of water at the surface of a silica glass. They suggested that water forms complexes with -OH bonds, where the -OH bonds are donors and the water molecules are acceptors of hydrogen bonds. For positrons tapped at the SiO_2/Si interface, they could form complexes with -OH bonds. The interaction between positrons and -OH bonds is considered to be similar to the hydrogen bonding.

4. CONCLUSIONS

We have studied the annihilation characteristics of positrons in the SiO_2 film and at the SiO_2/Si interface in the MOS specimen. Doppler broadening profiles of the annihilation radiation and lifetime spectra were measured as a function of incident positron energy for the poly-Si(100 nm)/SiO_2(400 nm)/Si specimen. In the SiO_2 film, the high formation probability of ortho-Ps was found. This can be attributed to the trapping of positrons by open-space defects in the SiO_2 film. The average lifetime of ortho-Ps in the SiO_2 film was determined as 1.5 ns. Applying the gate voltage between the poly-Si film and the Si substrate, positrons implanted into the SiO_2 film were accumulated at the SiO_2/Si interface. The value of I_2 was found to decrease with increasing the gate voltage. This result was attributed to the accumulation of positrons at the SiO_2/Si interface and the resultant inhibition of the Ps formation. At the SiO_2/Si interface, positrons are considered to form complexes with defects such as -OH bonds, and they annihilate with electrons before the formation of Ps.

REFERENCES

1. P. Hautojärvi (ed.), Positrons in Solids, Springer Topics in Current Physics Vol. 12, Springer-Verlag, Berlin, 1979.
2. P.J. Schultz and K.G. Lynn, Rev. Mod. Phys., 60 (1988) 701.
3. C. Corbel, P. Hautojärvi, J. Mäkinen, A. Vehanen and D. Mathiot, J. Phys. Condens. Matter., 1 (1989) 6315.
4. A. Uedono, L. Wei, Y. Tabuki, H. Kondo, S. Tanigawa and Y. Ohji, Mater. Sci. Forum, 105-110 (1992) 1475.
5. T.C. Leung, P. Asoka-Kumar, B. Nielsen and K.G. Lynn, J. Appl. Phys., 73 (1993) 168.
6. S. Dannefaer, Defect Control in Semiconductors, K. Sumino (ed.), North-Holland, Amsterdam, 1990, p.1561.
7. D.M. Schrader and Y.C. Jean (eds.), Positron and Positronium Chemistry, North-Holland, Amsterdam, 1988.
8. A. Uedono, S. Tanigawa, H. Funamoto, A. Nishikawa and K. Takahashi, Jpn. J. Appl. Phys., 29 (1990) 555.
9. R. Suzuki, Y. Kobayashi, T. Mikado, H. Ohgaki, M. Chiwaki, T. Yamazaki and T. Tomimasu, Jpn. J. Appl. Phys., 30 (1991) L532.
10. S. Berko, M. Haghgooie and J.J. Mader, Phys. Lett. A, 63 (1977) 35.
11. H. Ikari and K. Fujiwara, J. Phys. Soc. Jpn., 46 (1979) 92.
12. H. Nakanishi, S.J. Wang and Y.C. Jean, Positron Annihilation Studies of Fuids, S.C. Sharma (ed.), World Scientific Singapore, 1987, p. 292.
13. K. Klier, J.H. Shen and A.C. Zettlemoyer, J. Phys. Chem., 77 (1973) 1458.