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Growth of SiO_2 Thin Film by Photo-CVD Using 123nm VUV Light

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Good quality SiO_2 thin films were deposited on Si from the source gases of Si_2H_6 and O_2 by photo-CVD using selective excitation of the 123.6nm light from a Kr resonance lamp. The 123.6nm photon excites only Si_2H_6 but not O_2, and moreover may promote the surface reaction by photo-generated carriers. The amounts of Si-OH bondings in the SiO_2 films deposited by the 123.6nm light are much lower than those by the other VUV lamps. The interface state densities of the Si-MOS diodes are also remarkably reduced and its minimum value is $2x10^{10}cm^{-2}eV^{-1}$ near the Si mid-gap for the SiO_2 film deposited at the substrate temperature of 145°C.

§1. Introduction

Recently, much attention has been gathered on photo-induced chemical vapor deposition (Photo-CVD) for thin film preparation, because the deposition temperature can be reduced by the high-energy photon and the surface damage due to high-energy particles can be avoided. Many kinds of thin films such as Si[1], a-Si[2], SiO_2[3], and metals[4] have been prepared by photo-CVD. We have also tried to prepare SiO_2 films by photo-CVD using vacuum ultra violet (VUV) light from a D_2 lamp, and have shown that the VUV light irradiation is effective to prepare SiO_2 films having good electronic properties[5,6]. Recently, rare-gas resonance-lamps such as Xe or Kr lamp have been used to prepare a-Si[7] and Si_3N_4[8] thin films. Especially, the Kr resonance lamp has strong radiation at the wavelength of 123.6nm which is much shorter than those of the other VUV lamps. Therefore, the reactions by the Kr lamp are considered to be more activated than those by the other lamps, and various properties of SiO_2 thin films could be improved in photo-CVD using the Kr lamp. Furthermore, we took notice that the 123.6nm light is well absorbed by Si_2H_6 gas, but is hardly absorbed by O_2 gas. This selective excitation of the source gases is one of the advantages in direct photo-CVD, but, probably, has not yet been used positively. In this paper, we describe the results about the growth of SiO_2 thin films from O_2 and Si_2H_6 at very low temperature by the selective excitation using the Kr-resonance lamp.

§2. VUV Absorption of Source Gases

Figure 1 shows the absorption spectra of SiH_4, Si_2H_6[9] and O_2[10] in VUV light region. The strong radiation wavelengths of the VUV light sources are also shown by arrows in the upper part of Fig.1. The 123.6nm light from the Kr lamp is very adequate for the excitation of Si_2H_6, because Si_2H_6 has its maximum absorption around 120nm. Si_2H_6 absorbs about 125nm light and the higher transition ($1e_u \rightarrow 3d$) is induced than those by the Xe lamp ($1e_g \rightarrow 4s$) or the D_2 lamp

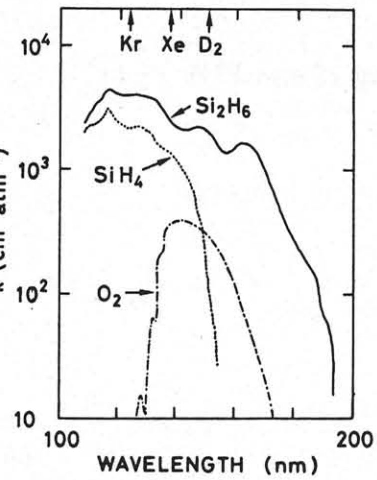

Fig. 1 Absorption coefficient spectra of SiH_4, Si_2H_6 and O_2 gases. Base is e. The radiation wavelengths of the D_2 lamp, Xe resonance and Kr resonance lamps are also shown by arrows.

($2a_{1g} \rightarrow 4s$). Si_2H_6 can be effectively decomposed to the radicals such as SiH, SiH_2 and SiH_3[11]. O_2 is hardly excited by the 123.6nm light because the absorption coefficient is less than $10cm^{-1}$. This indicates that the reaction between the non-excited O_2 and the silicon-hydride radicals is induced as a first photo-induced process. When the excited oxygen such as $O(^3P)$ reacts with Si_2H_6 molecule, it is considered that some reactions such as the insertion of O atom between Si and H atoms, the substitution and the scavenging occur. This insertion reaction makes Si-OH bondings. While in the case of the reaction between the non-excited O_2 and the silicon-hydride radicals, the dangling bonds of the radicals may react with O_2 molecules. It is expected that this reaction does not make the Si-OH bondings and that the amounts of the Si-OH bondings in the deposited films are reduced.

§3. Deposition of SiO_2 Films

Apparatus for photo-CVD process was almost the same as that reported in ref.5. The reaction chamber was a space between two quartz tubes and was evacuated by a turbo-

Table 1 Deposition Conditions

Reactant gases	O_2 and Si_2H_6
Gas flow rate ratio	0.23 (Si_2H_6/O_2)
Total gas pressure	27 Pa
Background pressure	2.7×10^{-4} Pa
Substrate temperature	25 - 300 °C

molecular pump before the deposition and by a rotary pump during the deposition. The Kr resonance lamp was set on the top of the reaction chamber and was excited by 2.45GHz microwave. Kr gas was diluted with He gas (Kr 10%), because it was reported by Okabe[12] that the radiation intensity of resonance lamps of rare gases such as Kr and Xe can be increased up several times by the dilution with He gas. Typical deposition conditions are shown in Table 1. The Xe resonance lamp and the D_2 lamp were sometimes used in order to study the difference of the film quality by the excitation energy.

Thicknesses and refractive indices of grown films were measured by an ellipsometer (Mizojiri DVA-36V-W) using 632.8nm light. Figure 2 shows the substrate temperature dependence of the growth rates. SiO_2 films did not grow without the irradiation of the

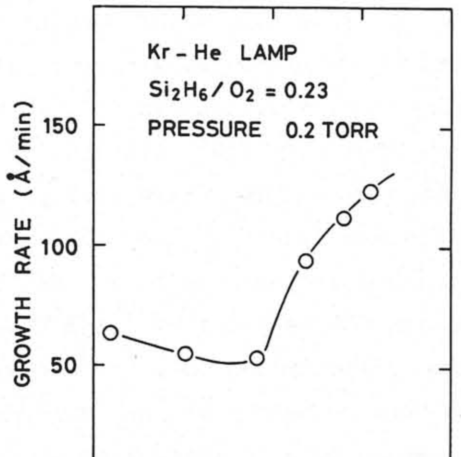

Fig. 2 Growth rate as a function of substrate temperature for the SiO_2 films deposited by photo-CVD.

Kr lamp at room temperature, but grew with the irradiation at a growth rate of about 60Å/min. This growth rate is smaller than those of the films deposited by the other VUV lamps because the light intensity of the Kr lamp is probably weaker than those of the others. Therefore, the increase of the intensity is necessary. The growth rate changes little with the substrate temperature below 200°C, but increases above 200°C. This indicates that the irradiation of the 123.6nm light is effective to grow films at low substrate temperature less than 200°C.

§4. Optical Properties

The refractive index of film deposited at 25°C is 1.39, but the indices increase with the substrate temperature and saturate above 145°C, 1.45-1.46, and are close to the thermally oxidized SiO_2 at 1000°C, 1.457.

Infrared (IR) transmission spectra were measured for the SiO_2 films by Fourier transformation infrared spectrometer (Japan Spectroscopic Co., Ltd., FT/IR-3). Figure 3 shows the IR spectra of the films deposited by the Kr lamp at 25°C and 100°C and by the

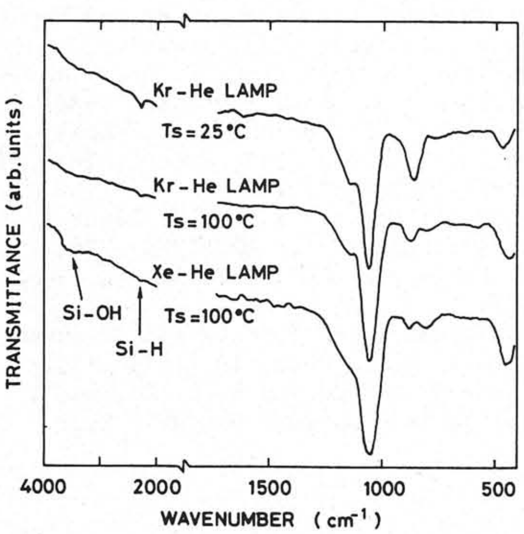

Fig. 3 Infrared transmission spectra of the films deposited by the Kr resonance lamp at 25°C and at 100°C and by the Xe resonance lamp at 100°C.

Xe lamp at 100°C. The absorption peaks corresponding to Si-OH ($3600cm^{-1}$) and Si-H ($2260cm^{-1}$) bondings exist in all three spectra, but these peaks decrease rapidly with the increase of the substrate temperature. The Si-OH peaks in the films deposited by the Kr lamp are smaller than those in the films by any other VUV lamp such as the Xe lamp. This is characteristic of the films deposited by the Kr lamp, and the Si-OH amount in the film deposited even at 25°C is much smaller than that by the Xe lamp at 100°C. The reason for the decrease of Si-OH is probably that the non-excited O_2 reacts with dangling bond of silicon hydrides decomposed by the 123.6nm light and is hardly inserted between Si and H atoms, as described in §2. The Si-H peaks in the films by the Kr lamp are larger then those by the Xe lamp. But it is expected that these peaks can be reduced by the increase of the light intensity of the Kr lamp.

§5. Electrical Properties

Electrical properties of Si-MOS diodes, which were made from the SiO_2 films of thickness about 1000Å, were measured. The C-V characteristics of the films deposited by the Kr lamp at low temperature of even 25°C can be measured, while those of the films by the other VUV light below 80°C cannot be measured because the breakdown voltage is small. Dielectric constants of the films deposited at 25°C are 5.5, and decrease with the substrate temperature.

Figure 4 shows the interface state densities measured by the DLTS method[13], Nss, of the Si-MOS diodes using the films deposited by the Kr lamp at 145°C and 200°C and by the Xe lamp at 235°C. The Nss by the Kr lamp is extremely low and its minimum density is about $2x10^{10}cm^{-2}eV^{-1}$ near the Si mid-gap for the film deposited even at low

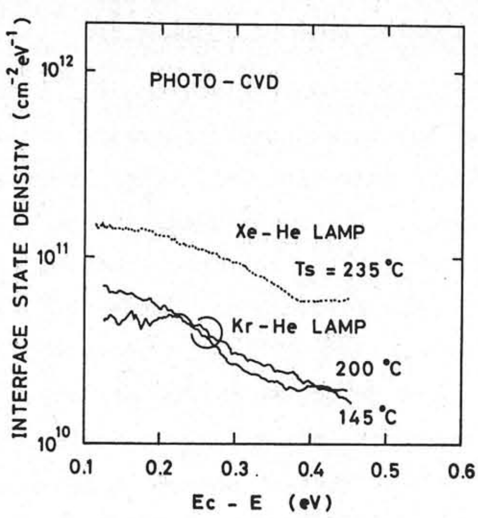

Fig. 4 Interface state density of the Si-MOS diodes using the SiO_2 films deposited by the Xe resonance lamp at 235°C and by the Kr resonance lamp at 200°C and at 145°C.

temperature of 145°C. The bandgap of SiO_2 is about 9eV and smaller than photon energy of the 123.6nm light (about 10eV) of the Kr lamp. So, the electron-hole pairs can be generated in the SiO_2 film and may promote surface reaction. This reaction accelerated on the surface may reduce the interface state. We measured the photo-conduction by the light of the wavelength above 110nm (below 11eV) of synchrotron radiation (SR), and Distefano and Eastman[14] obtained also photo-conduction which rise abruptly around 9eV.

§6. Summary

SiO_2 thin films were deposited by photo-CVD using the 123.6nm light of the Kr resonance lamp at the substrate temperatures between 25°C-300°C from Si_2H_6 and O_2. The growth rate is about 60Å/min at the substrate temperature of 25°C and does little change below 200°C but increases above 200°C. The IR absorption peaks of the Si-OH bonding in the films deposited by the Kr lamp are much smaller than those by the other VUV lamps. The interface state density, Nss, is also remarkably reduced by using the Kr lamp and its minimum value is about $2x10^{10}cm^{-2}eV^{-1}$.

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References

1) S. Nishida, T. Shiimoto, A. Yamada, S. Karasawa, M. Koganai and K. Takahasi ; Appl. Phys. Lett. **49** (1986) 79.
2) R. Bilenchi, I. Gianimoni and M. Musci ; J. Appl. Phys. **53** (1982) 6479.
3) Y. Mishima, M. Hirose and Y. Osaka ; J. Appl. Phys. **55** (1984) 1234.
4) T. F. Deutsch, D. J. Ehrlich and R. M. Osgood, Jr. ; Appl. Phys. Lett. **35** (1979) 175.
5) K. Inoue,, M. Michimori, M. Okuyama and Y. Hamakawa ; Jpn. J. Appl. Phys. **85** (1987) 805.
6) M. Okuyama, N. Fujiki, K. Inoue and Y. Hamakawa ; Jpn. J. Appl. Phys. **26** (1987) L908.
7) T. Fuyuki, K. Du, S. Okamoto, S. Yasuda, T. Kimoto, M. Yoshimoto and H. Matsunami ; to be published in J. Appl. Phys. August (1988).
8) K. Tamagawa, T. Hayashi and S. Komiya ; Preprints of the 46th Autumn Meeting of the Japan Society of Applied Physics, Kyoto, October, 1985, 2p-W-1.
9) U. Itoh, Y. Toyoshima, H. Onuki and N. Washida ; J. Chem. Phys. **85** (1986) 4867.
10) H. Okabe ; Photochemistry of Small Molecules (John wiley & Sons, Inc., New York) 1978, p.149.
11) G. G. A. Perkins and F. W. Lampe ; J. Am. Chem. Soc. **102** (1980) 3764.
12) H. Okabe ; J. Opt. Soc. Am. **54** (1964) 478.
13) Y. Yamasaki, M. Yoshida and T. Sugano ; Jpn. J. Appl. Phys. **18** (1979) 113.
14) T. H. Distefano and D. E. Eastman ; Solid State Commun. **9** (1971) 2259.