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Low Temperature Growth of Silicon Dioxide by Direct Photochemical Reaction of Si₂H₆ and O₂

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Silicon dioxide films have been prepared by the direct photolysis of disilane with oxygen even at a temperature of 150 °C. The deposition rate is remarkably increased by UV irradiation at temperatures below 300 °C, and correspondingly the activation energy is lowered down to 0.53 eV from 0.96 eV for conventional thermal CVD. The absorption peaks of the SiH and SiOSi stretching vibration of the matrix obtained by direct photo-CVD always appear at high wavenumbers as compared with those of thermal CVD films. This was interpreted in terms of the densification of the SiO₂ network by UV excitation during the deposition.

§1. Introduction

The photochemical decomposition technique utilizing mercury-photosensitization has recently been developed as a low temperature process technology for preparing Si_2 , $\mathrm{Si}_3\mathrm{N}_4$ and Si films.¹⁻⁴) For avoiding any mercury contamination in the deposition system, it is desired to develop an appropriate method to realize photo-CVD without employing mercury-photosensitization. Recently, we have demonstrated that hydrogenated silicon films can be deposited by direct photodissociation of $\mathrm{Si}_2\mathrm{H}_6$ using an Hg resonance lamp ($\lambda = 2537\mathrm{A}$, 1849 A).⁵)

In this paper, it is shown that the direct photochemical deposition of SiO_2 is achievable even at a temperature of 150 °C utilizing a Si_2H_6 + O_2 gas mixture. Vibrational spectra and dielectric properties of photo-CVD SiO_2 films are compared with those of thermal CVD SiO_2 to reveal the difference of the SiO_2 matrix prepared by the both techniques.

\$2. Experimental

A low pressure mercury-lamp(ll0 watts) as a UV radiation source was fixed just above a horizontal quartz reactor. Direct photo-CVD and thermal CVD were carried out at an atmospheric pressure. Silicon substrates were placed on a silicon susceptor heated with halogen lamps situated below the reactor. The flow rates of 1% disilane diluted with He and of pure oxygen are 200 cc/min and 600 cc/min, respectively, and a nitrogen carrier gas at a rate of 1500 cc/min was admixed.

§3. Results and Discussion

3-1 Deposition rate

The deposition rates of SiO_2 thin-films produced by the thermal CVD and direct photo-CVD of $Si_2H_6 + O_2$ are plotted in Fig. 1 as a function of reciprocal substrate temperature. The growth



Fig. 1 Growth rate of photo-CVD and thermal CVD films produced from $\text{Si}_{2}\text{H}_{6}$ + 0₂ against substrate temperature.

rate of silicon films obtained by direct photo-CVD was a constant at substrate temperatures below 350 °C,⁵⁾ whereas the deposition rate of SiO by photo- and thermal-CVD are activated with 0.53 eV and 0.96 eV, respectively, in the temperature range below 300 °C. This implies that the deposition rate of SiO_o is limited by the surface chemical reactions and remarkably enhanced by UV excitation, which lowers the activation energy. Similar phenomenon has also been observed in the vapor epitaxial growth of silicon. The activation energy of silicon deposition was decreased from 1.1 eV to 1.0 eV by light irradiation. 6) The growth rate of SiO, starts to decrease above 300 °C because gas phase reactions which result in formation of inert molecules becomes more important and effective flux density of film precursors towards the substrate surface is reduced.

3.2 Infrared spectra

The structural properties of SiO₂ deposited can be characterized by the vibrational spectra.⁷) The infrared spectrum of a photo-CVD SiO₂ is compared with that of a thermally oxidized SiO₂ at 1050 °C in Fig. 2. For a photo-CVD film, the six absorption peaks centered at 3500 cm⁻¹(SiOH stretching), 2265 cm⁻¹(SiH stretching), 1060 cm⁻¹ (SiOSi stretching), 930 cm⁻¹(SiOH deformation), 880 cm⁻¹ which is infered to be either due to $Si_2O_3^{(8)}$ or due to nonbridging SiO interaction,⁹) and 800 cm⁻¹(SiOSi stretching) are identified and basically common peaks are observed also for a thermal CVD sample. The SiO₂ film by the thermal



Fig. 2 Infrared absorption spectra of photo-CVD SiO_2 at a substrate temperature of 200 °C and of SiO_2 by the thermal oxidation of Si.

oxidation of Si shows only two peaks at 1080 cm⁻¹ and 800 cm⁻¹, both of which are ascribed to the SiOSi stretching vibration. Hydrogen related vibration and imperfect SiO bond vibration are absent because of the high temperature process. The integrated absorption intensities of the two peaks at 3500 and 930 cm⁻¹, which arise from SiOH bonds, are decreased by increasing the substrate temperature. This implies that the oxygen insertion reaction into SiH bonds on the growing surface becomes less important when the substrate temperature increases. Figure 3 shows the substrate temperature dependence of the ratio of the integrated absorption intensity due to the 880 wavenumber mode to 800 cm⁻¹ for thermal- and photo-CVD films.



Fig. 3 Substrate temperature dependence of the integrated intensity ratio of absorption at 880 cm^{-1} to 800 cm^{-1} .

It is decreased by increasing substrate temperature and by UV irradiation. This indicates that the SiO₂ network becomes more perfect by increasing substrate temperature and by illuminating UV light because the peak at 880 cm⁻¹, which is likely to arise from defects in SiO₂, is completely quenched in SiO₂ by the thermal oxidation of Si and because the 800 cm⁻¹ peak is characteristic for the stoichiometric SiO₂ network. Figure 4 represents the substrate temperature dependence of the peak wavenumbers of the SiH and SiOSi stretching modes. The absorption peaks of photo-CVD films always appear at higher wavenumbers with respect to those of thermal CVD

samples, regardless of substrate temperature. It is likely that photo-CVD films are more dense as compared with thermal CVD films, because the stronger molecular bond tends to provide the higher peak wavenumber of the stretching absorption.9) A significant shift of the peak wavenumber at temperatures above 300 °C could be attributed to a change in the deposition mechanism, in consistence with the result of Fig. 1. An increase of substrate temperature results in a shift of the SiH stretching absorption peak towards higher wavenumber possibly because the SiH bond length is changed by substrate temperature, ¹⁰⁾ while the peak wavenumber of the SiOSi stretching absorption at substrate temperatures above 300 °C moves to lower wavenumber presumably due to a change in the deposition mechanism, namely, the gas phase reaction is thought to be predominant above 300 $^{\rm o}{\rm C}$ instead of the surface reaction.



Fig. 4 Substrate temperature dependence of the peak position of the SiH and SiOSi stretching absorptions.

Indeed, the substrate temperature dependence of the integrated absorption intensities of the SiH and SiOSi stretching modes exhibits another evidence of a change in the deposition mechanism at temperatures below and above 300 °C (Fig. 5). The integrated SiOSi absorption intensities for both thermal and photo-CVD are almost identical, whereas

the SiH absorption intensity for photo-CVD is small as compared with that for thermal CVD over the whole substrate temperature range. This could be interpreted in terms of the presence of a hydrogen scavenging process on the growing surface, as suggested in the photochemical deposition of hydrogenated amorphous silicon.⁵⁾ The SiH absorption and SiOSi absorption start to increase at temperatures above 300 °C as a result of a change in the growth mechanism. When the specimen was annealed at 350 $^{\circ}$ C for an hour in a H $_{_{
m O}}$ atmosphere, the SiH integrated absorption intensity is reduced to about one half because of the hydrogen effusion irrespective of the deposition temperature of thermal- and photo-CVD samples, whereas, the SiOSi integrated absorption intensity is almost constant after annealing. This difference between SiH and SiOSi bonds might be associated with the result of Fig. 4, where the SiH stretching absorption peak moves to higher wavenumber and the SiOSi to lower by increasing the substrate temperature above 300 °C.



Fig. 5 Substrate temperature dependence of the integrated absorption intensities of the SiH and SiOSi stretching modes.

3.3 Electrical properties

We have measured 1 MHz C-V characteristics of MOS diodes fabricated from both thermal- and photo-CVD SiO_ films prepared at 200 $^{\circ}\mathrm{C}$ or 350 $^{\circ}\mathrm{C}.$ Ion-drift type hysterisis was observed and reduced by hydrogen annealing for specimens deposited at 350 °C. Despite significant difference in vibrational properties of thermal- and photo-CVD films prepared at 200 °C, there is no significant difference in the C-V characteritics. This will be due to the presence of a native oxide layer on a silicon substrate, which masks the difference of dielectric properties between thermal- and photo-CVD films. Also, the presence of SiOH will masks the difference because the hydrogen bonded to oxygen prevents the formation of SiOSi bonding. Figure 6 shows 1 MHz C-V characteristics for thermal- and photo-CVD SiO₂ films deposited at 350 °C. Both types of MOS diodes showed distinguishable properties, presumably because the electronic properties of native oxide on Si is improved at a higher substrate temperature and SiOH bonds are decreased at a higher substrate temperature.



Fig. 6 1 MHz capacitance - voltage characteristics of MOS diode fabricated from both thermaland photo-CVD SiO_2 which was deposited at 350 °C. The diodes were annealed at 350 °C for an hour in a H₂ atmosphere.

The mobile ion density estimated from the width of the hysteresis at the flat-band capacitance are $1.4 \times 10^{11} \text{ cm}^{-2}$ for thermal CVD and $7.7 \times 10^{10} \text{ cm}^{-2}$

for photo-CVD. The density of the fixed charge estimated from V_{FB} were $6 \sim 7 \times 10^{11}$ cm⁻² for thermal-CVD and $2 \sim 3 \times 10^{11}$ cm⁻² for photo-CVD. An appropriate in-situ cleaning of virgin silicon surface prior to CVD will be necessary for revealing the definite difference of dielectric properties of thermal- and photo-CVD SiO₂.

§4. Conclusion

The direct photochemical deposition of SiO_2 by UV excitation of a $\text{Si}_2\text{H}_6 + \text{O}_2$ gas mixture is achievable at low temperatures without employing any mercury photosensitization. Implication of the densification of the SiO_2 network by photo-CVD was obtained from the result of the vibrational spectra and C-V characteristics. The direct photo-CVD process appears to be promissing as a low temperature process to grow SiO_2 without any Hg contamination.

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