

## VI-M Thin Film Preparation with Chemical Vapor Deposition Using Vacuum Ultraviolet Radiation

Thin-film deposition at temperatures as low as possible is one of the key technologies for next generation of ultra-large scale integrated circuit (ULSI) fabrication. Photon-assisted chemical vapor deposition is a promising way to prepare particularly dielectric thin films. Silicon dioxide and germanium dioxide films have been prepared from tetraethoxysilane ( $\text{Si}-(\text{OC}_2\text{H}_5)_4$ ) and tetraethoxygermanate ( $\text{Ge}-(\text{OC}_2\text{H}_5)_4$ ) with chemical vapor deposition using vacuum ultraviolet radiation.

### VI-M-1 Design and Construction of UVSOR-BL4A2 Beam Line for Nano-Structure Processing

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Nano structures must open new windows not only for surface physics and chemistry but also for electronic and photonic devices. Synchrotron radiation stimulated surface chemical reactions have been a most promising way to fabricate nano structures, because they offer a process with the advantages of high-site selectivity by core electron excitation and also free-of damage with atomic scale. Since a new beam line with higher flux is required for the processing, we have been designing and constructing UVSOR-BL4A2 beam line for the nano structure fabrication.

### VI-M-2 Characterization of $\text{SiO}_2$ Dielectric Films in Photo-Chemical Vapor Deposition Using Vacuum Ultraviolet Excimer Lamp

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[199<sup>th</sup> Meeting of Electrochemical Society **241**]

Photo-chemical vapor deposition using vacuum ultraviolet excimer lamp is a novel technology that deposit  $\text{SiO}_2$  film at room temperature without the use of high temperature or plasma. The films contain organic impurities coming from tetraethoxysilane (TEOS) used as the precursor. The addition of  $\text{O}_2$  molecules to TEOS is found to decrease C–H impurities. We show atomic concentrations in  $\text{SiO}_2$  films deposited from TEOS or from TEOS with  $\text{O}_2$  or  $\text{N}_2\text{O}$  gas.

### VI-M-3 Electrical Properties of $\text{SiO}_2$ films Prepared by VUV Chemical Vapor Deposition

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[199<sup>th</sup> Meeting of Electrochemical Society **257**]

We have developed a new scheme for  $\text{SiO}_2$ -film preparation in which tetraethoxyorthosilicate (TEOS:  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ) is photo-dissociated by vacuum ultraviolet  $\text{Xe}_2$  excimer radiation ( $\lambda = 172$  nm) at room temperature. The  $\text{SiO}_2$ -films are included impurities of C and H atoms and/or molecules. A adding foreign gases included O atom and molecule to TEOS are effective in removal of C atom and/or molecule in  $\text{SiO}_2$ -film, which bring about excellent gap-filling property, but it is newly included OH impurity. We had knowledge that the electrical properties of  $\text{SiO}_2$ -films is correlated the amount of OH impurity by FT-IR spectra, C–V and I–V curves. Increase of OH impurity is degraded electrical properties. An only TEOS have not OH impurity, which may be using as the low-k films of next future device processes.

### VI-M-4 $\text{SiO}_2$ Film Deposition on Different Substrate Materials by Photo-CVD Using Vacuum Ultraviolet Radiation

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[199<sup>th</sup> Meeting of Electrochemical Society **258**]

We have prepared  $\text{SiO}_2$  thin films from tetraethoxyorthosilicate (TEOS) at room temperature by photo-chemical vapor deposition using a vacuum ultraviolet (VUV) excimer lamp. We showed the affection by adding foreign gases to the raw precursor and by changing substrate materials for the growth rate and thickness uniformity and the reaction mechanism by step coverage in VUV-CVD. The  $\text{SiO}_2$  film deposition behaviors by VUV-CVD depend significantly on the presence of ozone and activated oxygen by VUV photons. Then the dependence of substrate materials for the growth rate and thickness uniformity is most remarkable in case of adding  $\text{O}_2$ .

### VI-M-5 Silica Film Preparation by Chemical Vapor Deposition Using Vacuum Ultraviolet Excimer Lamps

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We have prepared SiO<sub>2</sub> thin films on silicon wafers from tetraethoxyorthosilicate (TEOS; Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>) by photo-chemical vapor deposition (photo-CVD) with the use of various excimer lamps which emit incoherent light at 308 (XeCl), 222 (KrCl), 172 (Xe<sub>2</sub>), 146 (Kr<sub>2</sub>) and 126 nm (Ar<sub>2</sub>). The film deposition is observed at wavelengths shorter than 172 nm. With 10-mW/cm<sup>2</sup> 172-nm radiation, the growth rate is 8 nm/min on the room temperature substrate. The deposition efficiency depends on the wavelength and shows the maximum value for 146-nm radiation. Addition of O<sub>2</sub> to TEOS induces inhibition of C and H impurity inclusion in the films.

### VI-M-6 GeO<sub>2</sub> and SiO<sub>2</sub> Thin Film Preparation with CVD Using Ultraviolet Excimer Lamps

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We have prepared SiO<sub>2</sub> and GeO<sub>2</sub> thin films from tetraethoxyorthosilicate (TEOS; Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>) and tetraethoxyorthogermanate (TEOG; Ge(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>), respectively, by chemical vapor deposition (CVD) assisted by high-energy photons. The photons are supplied from excimer lamps which emit incoherent light at 308 (XeCl), 222 (KrCl), 172 (Xe<sub>2</sub>), 146 (Kr<sub>2</sub>) and 126 nm (Ar<sub>2</sub>). GeO<sub>2</sub> film deposition is observed for all excimer lamps used here, but SiO<sub>2</sub> films are obtained at wavelengths shorter than 172 nm. This is caused by a fact that the bonding energy between Si and O is much higher than that between Ge and O. The deposition rate is around 8nm/min for SiO<sub>2</sub> and 16nm/min for GeO<sub>2</sub> films. The film deposition rate increases with increasing the light intensity and with decreasing substrate temperature.

### VI-M-7 Room Temperature Deposition of GeO<sub>2</sub> Thin Films Using Dielectric Barrier Discharge Driven Excimer Lamps

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We discuss the fabrication of GeO<sub>2</sub> and GeO<sub>2</sub>/SiO<sub>2</sub> films at room temperature by photo-chemical vapor deposition. Excimer lamps were used for the light source, and tetraethoxyorthosilicate (TEOS) and tetraethoxyorthogermanate (TEOG), as raw materials. We fabricated GeO<sub>2</sub>/SiO<sub>2</sub> composite films from a mixed vapor of TEOS and TEOG. The refractive indices of the obtained films showed intermediate values between those of SiO<sub>2</sub> ( $n = 1.46$ ) and GeO<sub>2</sub> ( $n = 1.60$ ). The relationship between Ge concentration in the films and the refractive indices was examined. We successfully obtained a GeO<sub>2</sub>/SiO<sub>2</sub> composite material of higher refractive index than that of similar composites produced by conventional methods.