VI-M Thin Film Preparation of SiO_2 by Photo-Chemical Vapor Deposition Using Vacuum Ultraviolet Radiation

Silicon dioxide has been extensively used and studied in semiconductor manufacturing applications. For such a material, conventional pyrolytic deposition occurs above 600 °C while traditional oxidation occurs at temperatures around and above 900 °C. Low temperature processing has become much more important mainly in the semiconductor industry, according to the continued reduction in device geometry. Photo-stimulated processing is very promising since the processed surfaces and growing films are not subjected to damaging ionic bombardment unavoidable in plasma-assisted processing systems. The aims of this project are to exploit the fundamental processes and to demonstrate the possibility and inherent advantages of depositing silicon dioxide at room temperature from tetraethoxyorthosilicate (TEOS: $Si\text{-}(OC_2H_5)_4$) with the use of vacuum ultraviolet radiation.

VI-M-1 SiO_2 Thin Film Preparation Using Dielectric Barrier Discharge-Driven Excimer Lamps

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[*Appl. Surf. Sci.* **138-139**, 340 (1999)]

By suing a photochemical vapor deposition method with a Xe_2 excimer lamp (172 nm, 20 mW/cm^2 output power), silica films have been prepared by means of a single precursor from tetraethoxyorthosilicate (TEOS) at room temperature. Transparent thin films of SiO_2 obtained on sapphire and quartz single crystal substrates with a deposition rate of 0.9 nm/min. They were mainly composed of amorphous SiO_2, although small amounts of residual organic materials were contained. The refractive index was 1.476 at 632.8 nm. The surface roughness decreased with the film thickness and reached 0.2 nm-rms. These findings indicate that the VUV excimer lamp CVD is a promising method for preparing smooth, dense and fine thickness-controllable films of SiO_2 at room temperature.

VI-M-2 SiO_2 Film Coatings with VUV Excimer Lamp CVD

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[*Mater. Res. Soc. Symp. Proc.* **555**, 167 (1999)]

Silica film coatings were demonstrated using photo-chemical vapor deposition with a 172-nm Xe excimer lamp. Tetraethoxyorthosilicate (TEOS) molecules were successfully dissociated into $SiO_2 + 2C_2H_5\text{-}OH$ + (residual C and H) with the 7.2-eV photons. The films were deposited onto quartz or Al_2O_3 single crystal substrates with the deposition rate of 1 nm/min. The films were uniform and smooth enough for optical applications.

VI-M-3 Thin Film Preparation Using Vacuum Ultraviolet Rare Gas Excimer Lamps

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[Hyomen Kagaku 20, 401 (1999)]

Rare gas excimer lamps using dielectric-barrier discharge are new type of compact and high-efficient light source for vacuum ultraviolet wavelength region. Since the lamps produce incoherent and quasi-continuous radiation, uniform processing over large sample areas is expected to be possible without thermal effects and speckling or interference fringes. The purpose of this paper is to exploit a new technique of material processing by use of the newly developed incoherent rare gas excimer lamps. We will describe some findings obtained by applying the excimer lamps to preparation of silica films. A photochemical vapor deposition using Xe_2* excimer lamp has made it possible to prepare silica films by means of a single precursor process from tetraethoxyorthosilicate (TEOS) at room temperature. Transparent SiO_2 thin films were obtained with a deposition rate of 0.9 nm/min. The refractive index was 1.476 at 632.8 nm and the surface roughness reached 0.2 nm-rms. These findings indicate that the VUV excimer lamp CVD is promising method for preparing smooth and fine thickness-controllable films of SiO_2 at room temperature. We confirmed that this technique provides a very promising photo-quantum process for the fabrication of semiconductors and opt-electronic devices, and others.

VI-M-4 Photo-Dissociation Process of Tetra-ethoxyorthosilicate (TEOS) Induced by Synchrotron Radiation

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Tetraethoxyorthsilicate (TEOS: $Si\text{-}(OC_2H_5)_4$) is one of the promising materials for preparing insulating SiO_2 thin layer in semiconductor industry. Photo-chemical vapor deposition using vacuum ultraviolet radiation provides the thin film preparation at room temperature. However the photo-dissociation process has never been exploited yet. We have a plan to exploit the detailed process, to find the most appropriate conditions, in particular for wavelength, and to make high quality SiO_2 thin film using synchrotron radiation (at the beam lines of BL-1B and BL-7B of UVSOR).

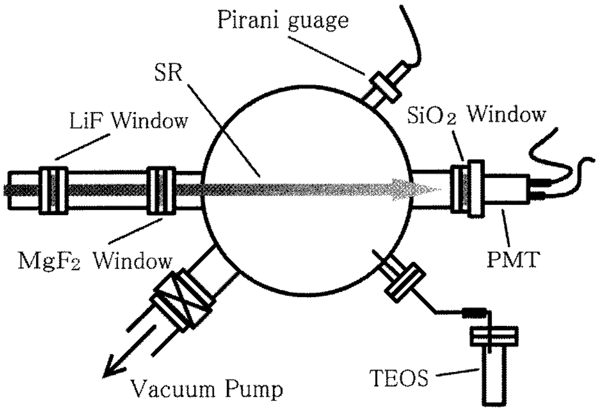

Figure 1. Schematic drawing of reaction chamber for TEOS.

VI-N Vacuum Ultraviolet Lasers and Their Applications to Surface Modification of Silica Glass

Rare gas excimers are most promising materials for coherent light sources in vacuum ultraviolet spectral region. Among them, an argon excimer laser which provides 126-nm photons has been realized only by high-energy electron beam pumping. The photon energy surmounts the band-gap energy of almost all solid-state materials and thus has a strong interaction with the materials. For an example, we have demonstrated that the 9.8-eV photons excite electrons from the valence band to the conduction band via one-photon process, resulting in desorption of oxygen atoms and crystal growth of silicon in the surfaces of silica glass and quartz crystals.

VI-N-1 The State of the Art of Rare Gas Excimer Lasers and Lamps as a Light Source for Giga-Bit Lithography

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[*J. Photopolymer Sci. Tech.* **11**, 361 (1998)]

Coherent and incoherent light sources using rare gas excimers are reviewed from a point of view of post ArF lithography. Present status of electron beam pumped rare gas excimer lasers is reported. Potentialities of rare gas excimer lasers by discharge pumping are discussed. We have obtained laser gain of 2.2×10^{-3} cm^{-1} in Kr discharge that was very close to the threshold gain. It is pointed out that gas excimer lasers are suitable for light sources for next generation lithography after ArF lithography in the 21st century, when a compact excitation method is established. Jet discharge excimer lamps are also discussed from a point of view of an incoherent light source for lithography.

VI-N-2 Radiation Effects of Vacuum Ultraviolet Lasers on Silica Glasses

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[*J. Photopolymer Sci. Tech.* **11**, 367 (1998)]

Excimer-laser processing can be extended to a broader and more diverse range of materials by moving to vacuum-ultraviolet (100–200 nm) laser sources such as the molecular fluorine and argon excimer lasers. The 126-nm and 157-nm output wavelengths from the argon excimer and fluorine lasers take advantages of the extremely high photon-energy, the high opacity in most materials, and short pulse duration to minimize thermal loading of target surfaces. The lasers readily drive photochemical interactions. The 126-nm photons induce oxygen desorption and silicon precipitation both in high purity silica glass and crystalline quartz. The 157-nm photons readily etch off the surfaces in vacuum ultraviolet-grade silica glass and crystalline quartz.

VI-N-3 X-Ray Emission Spectroscopic Studies of Silicon Precipitation in Surface Layer of SiO_2 Induced by Argon Excimer Laser Irradiation

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[*Appl. Surf. Sci.* **126**, 83 (1998)]

The ultra-soft X-ray emission spectra were taken from surfaces of bulk silica glass and silica glass films exposed to an argon excimer laser (λ = 126 nm) and composed with the spectra taken from the virgin surfaces. The precipitation of crystalline silicon is found to take place in thin surface layers of the irradiated bulk silica glass and 15 nm film. An estimation of concentration of crystalline silicon precipitation with the depth is given on the basis of the measurements of Si $L_{2,3}$ X-ray emission spectra obtained at different accelerating voltages of the electron beam on the X-ray tube. Based upon the precipitation conditions for these samples, we discuss the crystalline silicon precipitation mechanisms: the electronic excitation induces the bond-breaking between Si and O atoms, although there is a critical density of photons for the bond-breaking and temperature rise enhances the crystalline silicon precipitation.

VI-N-4 Polycrystalline Silicon Precipitation on SiO_2 Using an Argon Excimer Laser

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[*Appl. Surf. Sci.* **137**, 78 (1999)]

We are developing an argon excimer laser that oscillates at 126 nm (9.8 eV). Since the photon energy of the laser is as high as 9.8 eV, the laser can induce bond breaking in most of materials without any reactive gas or solution. We performed irradiation of an argon excimer laser on crystal and glass SiO_2, and then investigated the surfaces by means of X-ray photo-electron spectroscopy, Raman scattering, X-ray diffraction and reflection of high-energy electron diffraction measurements. The results indicate that polycrystalline silicon precipitates on the surface with a preferential orientation.

VI-O Photo-Stimulated Luminescence as Data Storage in UV to Vacuum UV Regions

Photo-stimulated luminescence is a promising process for data storage in X-ray radiation with the advantages of linear response and wide dynamic range. The fundamental mechanisms under the data storage in imaging plates using BaFBr:Eu as the photo-stimulated luminescence material have been explained to trapping electrons released from Eu impurity atoms at least for X-ray radiation. Viewing the energy diagram, we can expect the photo-stimulated process occurring even for Vacuum UV and UV radiation. We have exploited the fundamental mechanism for data storage in the imaging plate particularly for VUV and UV radiation.

VI-O-1 Response Characteristics of Imaging Plate in UV Region

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[*Rev. Laser Eng.* **26**, 812 (1998)]

An imaging plate (IP) has been developed as an image-storing medium for use in medical X-ray diagnosis. We confirmed the IP to be a good medium not only for X-ray radiation but also vacuum ultraviolet (VUV) and ultraviolet (UV) radiation. We found that the photo-stimulated luminescence (PSL) intensity showed a linear response to UV photon numbers in the range of $10^{4.5}$, and that showed saturation as the irradiated photon number increased. The sensitivity curve of the IP showed a peak at the wavelength of 200 nm and decreased at longer wavelengths. When the wavelength of the irradiated UV radiation was longer than 320 nm, the PSL intensity was too low to detect with our system. This means that the cut-off wavelength of the sensitivity was measured as 310 nm.

VI-P Nano-Structure Fabrication Using Synchrotron Radiation Stimulated Processing

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 processings, we have been designing and constructing BL-4A2 beam line for the nano structure fabirication.

VI-P-1 Design and Construction of BL-4A2 Beam Line for Nano-Structure Processing

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([1]Miyazaki Univ.; [2]Himeji Inst. Tech.; [3]Toyohashi Univ. Tech.)

We have been constructing a new beam line BL-4A2 which consists of white ray beam, ultra-high vacuum scanning tunneling microscope (UHV-STM) and photo-stimulated reaction chamber. In near future, we are going to join a near field optical microscope for monitoring optical properties with the atomic scale to them. Figure 1 shows the outline of the beam line, which consists of pre-focusing mirror (M1), secondary mirror (M2), monitor port, two differential pumping ports, reaction chamber and STM. An elliptically bent cylindrical mirror made of a quartz coated with platinum is used as the pre-mirror. The reflected beam is focused at a point of 12.7 m down stream from the center of the pre-mirror and has a sopt size of 8 × 6 mm^2. Low energy electron diffraction (LEED) is installed in the reaction chamber for in-situ characterization of substrate surfaces and also STM is for observation of the surface processes with atomic scale. We have a plan to make a photonic band-gap structures in a SiO_2 planer waveguide and study evanescent light from the waveguide surfaces with near field optical microscope.

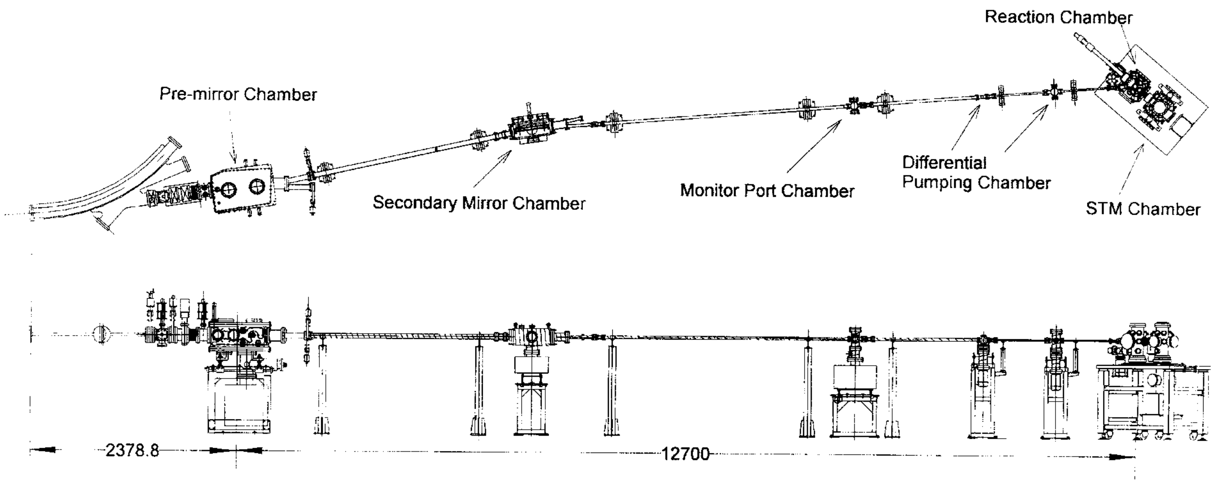

Figure 1. Schematic drawings of the BL-4A2 beam line with a reaction chamber and STM.