VI-F Synchrotron Radiation Stimulated Surface Reactions

Study of synchrotron radiation (SR) stimulated surface reaction is a promising topic in fundamental science, because dynamical processes induced by the photostimulated coreelectron excitations on surfaces are scarcely explored so far. This field is important also in applied science, since the fundamental study is expected to develop the new techniques for semiconductor processing such as SR stimulated etching and SR stimulated epitaxial growth.

VI-F-1 Vibration Analysis of SiH_n Bending Modes on Hydrogenated Si(100) Surface Using Infrared Reflection Absorption Spectroscopy

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Detailed analyses have been successfully made for the SiH_n stretching vibration mode on hydrogenated Si(100) surface, which is of great scientific and technological interest.[1)] However, concerning the bending vibration region, which gives important information about SiH_2 and SiH_3 species, very little work has been done. Recent developments of buried metal layer-infrared reflection absorption spectroscopy (BML-IRRAS) have made the high-resolution vibration analysis of the bending region easy. In this work, adsorption and desorption of hydrogen on Si(100) surfaces have been investigated by measuring BML-IRRAS covering a wide spectral range (800–2200 cm^{-1}). In both 3×1 and 1×1 phases observed with reflection high-energy electron diffraction (RHEED), a doublet peak (902 and 913 cm^{-1}) has been clearly observed and assigned to the SiH_2 scissors mode. The splitting of the peak is most likely due to the frequency difference of SiH_2 scissors vibration between single SiH_2 (ordered 3×1 units; H-Si-Si-H H-Si-H H-Si-Si-H) and neighboring SiH_2 (disordered 3×1 units; H-Si-Si-H H-Si-H H-Si-H H-Si-Si-H). Coverage and annealing temperature dependence of this doublet peak have also been investigated.

Reference

1) Y. J. Chabal and K. Raghavachari, *Phys. Rev. Lett.* **54**, 1055 (1985).

VI-F-2 Scanning Tunneling Microscopy for the Study of the Synchrotron-Radiation Stimulated Processes; Synchrotron-Radiation Stimulated Desorption of SiO_2 Films on Si(111) Surface

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[*Jpn. J. Appl. Phys.* **38**, 249 (1999)]

We have constructed a scanning tunneling microscopy (STM) system for the study of synchrotron radiation (SR) stimulated photochemical reactions. In order to eliminate the vibration and acoustic noise, the entire UHV chamber is mounted on a high-performance air-suspended vibration isolation table and was also covered by the soundproof mat. The mechanisms for SR stimulated desorption of SiO_2 thin films on the Si (111) surfaces have been investigated using the STM, low energy electron diffraction (LEED) , and Auger electron spectroscopy. An atomically flat and clean Si(111)-(7×7) surface was obtained after two hours SR irradiation at a surface temperature of 700 °C. The STM topograph suggests that the desorption mechanism may be completely different between thermal and SR stimulated desorption of SiO_2 film.

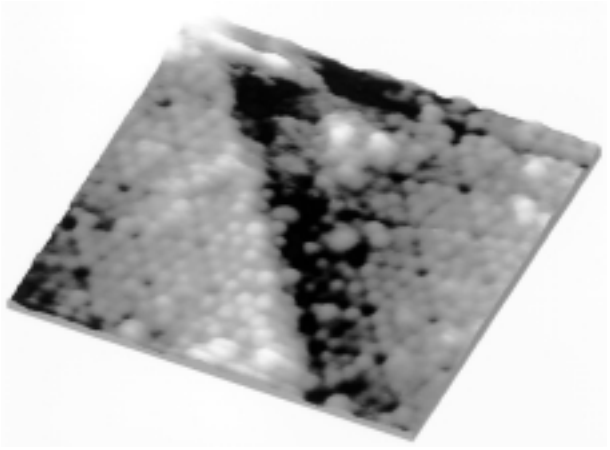

Figure 1. Three-dimensional STM image of 2 hours SR-irradiation to the samples at the sample temperature of 700 °C. Image size = 15 × 15 nm.

VI-F-3 Synchrotron-Radiation Stimulated Desorption of SiO_2 Thin Films on Si(111) Surfaces Observed by Scanning Tunneling Microscopy

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[*J. Vac. Sci. Technol., A* **17**, 1733 (1999)]

Synchrotron radiation (SR) stimulated desorption of silicon dioxide thin films was studied using scanning tunneling microscopy (STM) , low energy electron diffraction (LEED) , and Auger electron spectroscopy. Reconstructed Si(111)-7×7 patterns were observed by LEED after 2 h SR irradiation at a surface temperature of 700 °C. The STM images show an atomically flat Si(111)-(7×7) surface. STM topographs of SR-irradiated surfaces suggest that the oxide desorption mechanism is completely different from that of thermal desorption of SiO_2 film. These results indicate that the atomically flat Si surface can be obtained at low temperatures by using this technique.

VI-F-4 Direct Observation of Synchrotron Radiation Stimulated Desorption of Thin SiO_2 Films on Si (111) by Scanning Tunneling Microscopy

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[*Surf. Sci. Lett.* **437**, L755 (1999)]

This is the first report of the use of scanning tunneling microscopy (STM) to study changes in the surface morphology during synchrotron radiation (SR) stimulated desorption of SiO_2 films on Si(111). An atomically flat surface was obtained after two hours SR irradiation at a surface temperature of 700 °C. The STM topograph indicates that the SR desorption mechanism is quite different for the thermal desorption of SiO_2. The non-formation of multistep holes on the exposed Si surface indicates that the desorption of oxygen atoms and molecules by SR excitation leaving volatile SiO is an important mechanism.

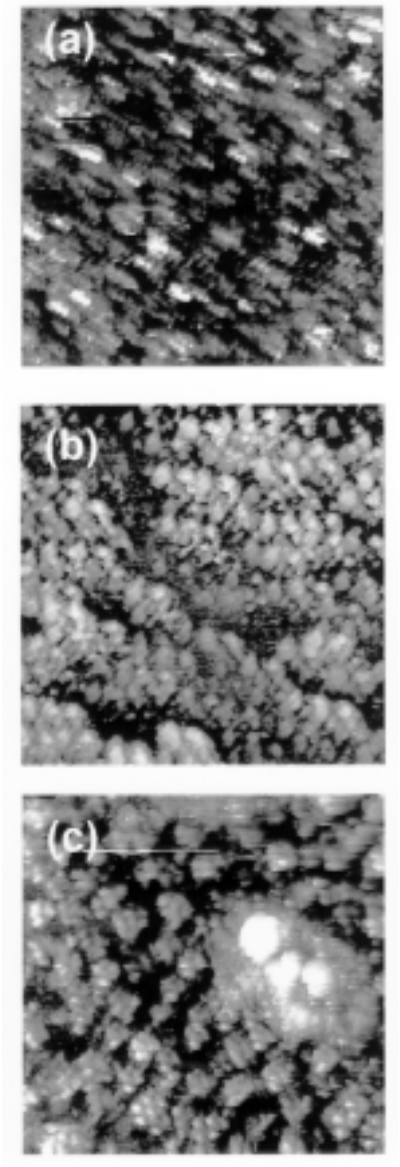

Figure 1. (a) STM image of Si (111) sample after 2.5 h SR-irradiation at the sample temperature of 650 °C. Image size = 2000 × 2000 Å. (b) STM image of 1 h SR-irradiation to the samples at the sample temperature of 700 °C. Image size = 5000 × 5000 Å. (c) STM image of 2 h SR-irradiation to the samples at the sample temperature of 700 °C.

VI-F-5 Scanning Tunneling Microscopy Study of Surface Morphology of Si(111) after Synchrotron Radiation Illumination

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The surface morphology of Si(111) was investigated using scanning tunneling microscopy the after illumination by synchrotron radiation. The surface shows large regions of atomically flat Si(111)-7×7 structure, and is characterized by the formation of bilayer atomic steps nicely registered to the crystal structure. The pinning of the steps by nanometer scale dust sis evident. This is in sharp contrast to Si(111) surfaces after thermal desorption of SiO_2 at temperatures 880 °C and above, where the surface steps are much more irregular. The registration of the surface steps to the underlying crystal structure indicates that the bilayer atomic steps reach thermodynamic equilibrium under synchrotron radiation at temperatures much lower than that necessary for thermal desorption.

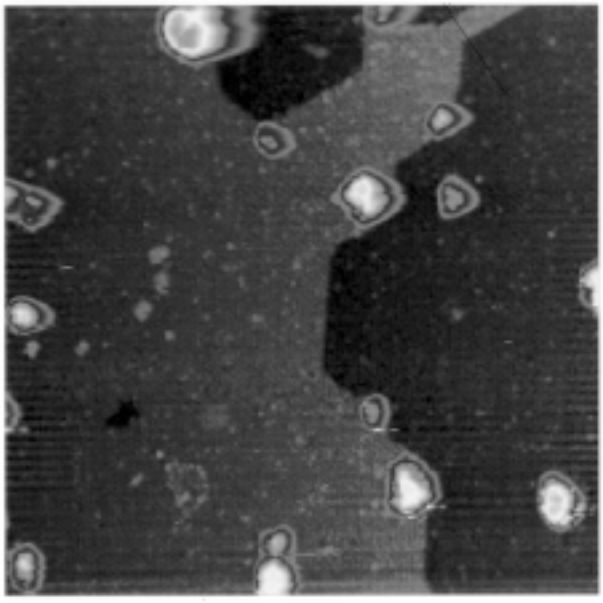

Figure 1. 1000 × 1000 $Å^2$ topograph of a Si(111) surface after 5 hours of SR irradiation at 650 °C. The most striking feature of the topography is the bilayer steps in alignment to the high symmetry axes of the surface.

VI-F-6 Construction of the Multilayered-mirror Monochromator Beam Line for the Study of Synchrotron Radiation Stimulated Process

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[*Rev. Sci. Instrum.* **70**, 2601 (1999)]

A multilayered-mirror (MLM) monochromator beam line designed specially for synchrotron radiation (SR) stimulated process experiments has been constructed for the first time. The beam line was designed by the criteria ; a beam spot size on the sample surface ≥ 3 × 3 mm^2, a density of total irradiated photons ≥ 10^{18} photons/cm^2 (for an irradiation time of a few tens of minutes to a few hours) and low-energy background ≤ 1% of the output. The performance of the beam line was evaluated by measuring the transmitted photon flux of an Al filter around the Al $L_{2,3}$ absorption edge and by measuring the photo-emission spectra of Ta using the output beam as an excitation light source. The Al thin film deposition was successfully demonstrated by using the monochromatized output beam. We conclude that this MLM monochromator performs sufficiently well to study the excitation energy dependence in SR-stimulated processes.

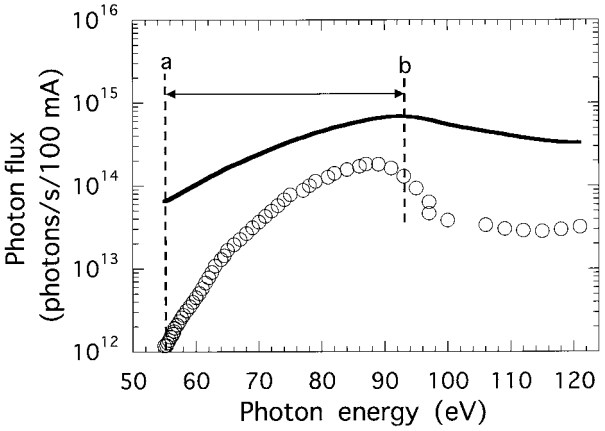

Figure 1. The dependence on the photon energy of the photon flux of output beam. The solid line shows calculated values and "○" shows measured values. The dotted lines a and b show the working region of the monochromator.

VI-F-7 Excitation Energy Dependence on Composition of an Al Deposited-thin Film Stimulated by Monochromatized SR

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The output beam of a multilayered-mirror monochromator beam line (BL4A1) at the UVSOR of the IMS was applied to an Al thin film deposition using dimethylaluminum hydride (DMAH) low temperature condensed layer. After cooling Si(100) substrate to about 100 K, the DMAH gas was introduced and deposited on the substrate (10–20 monolayers). The surface of the substrate was irradiated by the monochromatized SR beam tuned to the Al 2p core electron excitation energy, and the composition of the deposited film was measured by XPS at room temperature. An interesting point is the C concentration of the deposited film. By assuming C/Al = 2 for DMAH condensed layer before irradiation, the minimum composition C/Al of the deposited film is estimated to be about 0.65. This value is quite small compared with those of films obtained by the white or filtered white SR beams irradiations. This may be due to that the Al-C bond is preferentially broken by the Al core electron excitations.

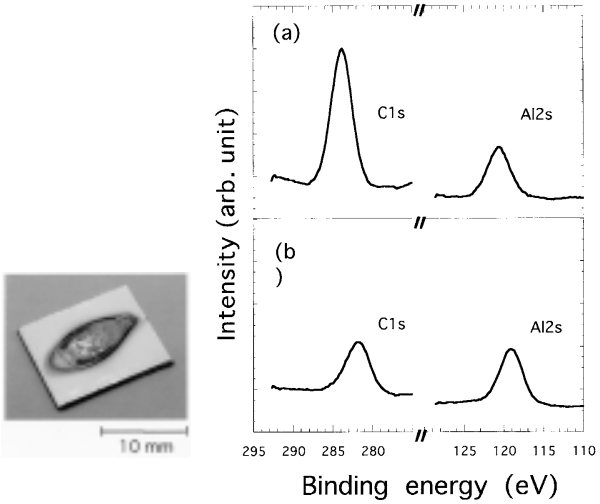

Figure 1. Photograph of the deposited Al thin film and the observed XPS spectra for (a) the DMAH condensed layers at 105 K and (b) the deposited Al thin film.

VI-F-8 SR-stimulated Etching and OMVPE Growth for Semiconductor Nano-structure Fabrication

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We proposed a new method to form ordered array of the quantum dots using SR-stimulated etching and selective area growth by OMVPE. The SR etching has a great potential for fabrication of semiconductor devices, because side wall is very vertical and the induced damage of the etched surface is extremely low. Neither of them can be achieved by wet chemical etching or RIE. We report here preliminary results on SR etching of SiO_2 on InP substrate and growth of InP on the patterned substrate. SR etching was performed by exposing SiO_2 to SR irradiation in SF_6 ambient. The etched depth dependence on SF_6 pressure ranging from 5×10^{-8} Torr to 0.5 Torr was investigated at SR irradiation dose of 10,000 mA·min. The maximum etching rate in this study was 4.7×10^{-3} nm/(mA·min) at SF_6 pressure of 0.05 Torr. Using the SR etching, we patterned SiO_2 with 0.4 μm opening on the InP substrate. Selective area growth of InP was successfully observed on the patterned substrate. In the low-temperature PL measurement, exciton related emission lines were clearly observed.

VI-G Ion Desorption Induced by Core-Electron Transitions Studied by Electron Ion Coincidence Spectroscopy Combined with Synchrotron Radiation

Ion Desorption Induced by Core-Electron Transitions has been studied using energy-selected electron ion coincidence spectroscopy combined with synchrotron radiation. Auger electron photo-ion coincidence (AEPICO) and photoelectron photo-ion coincidence (PEPICO) spectroscopy proved to be an ideal tool for investigations of the ion desorption induced by core-level excitations. AEPICO results show that the character of the orbitals where holes are created, as well as the effective hole-hole Coulomb repulsion are important factors in the Auger-stimulated ion desorption from covalent molecules. The PEPICO spectroscopy, on the other hand, provided direct evidences of site-specific ion fragmentation induced by core-level excitations.

VI-G-1 Study of Ion Desorption Induced by a Resonant Core-Electron Transition of Condensed H_2O by Using Auger Electron Photoion Coincidence (AEPICO) Spectroscopy Combined with Synchrotron Radiation

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Proton desorption mechanism in the region of resonant excitations of Oxygen 1*s* core-electron of condensed water is studied using Auger electron photoion coincidence (AEPICO) spectrometer with an improved resolution of the electron kinetic energy of $E/\Delta E$ = 100. The spectrum of total ion yield divided by Auger electron yield (AEY, electron kinetic energy: 490 eV) exhibited a characteristic threshold peak at the $4a_1 \leftarrow$ O:1*s* resonance ($h\nu$ = 532.3 eV) and a suppression at the $3p \leftarrow$ O:1*s* resonance ($h\nu$ = 535.5 eV). The electron kinetic energy dependence of the AEPICO yield (AEPICO yield spectra) were measured at $h\nu$ = 532.6, 533.6, 335.4, 540.6, 547.6 and 557.8 eV. At the $4a_1 \leftarrow$ O:1*s* resonance ($h\nu$ = 532.6 eV) and $2b_2 \leftarrow$ O:1*s* resonance ($h\nu$ = 533.6 eV), the AEPICO yield spectrum exhibited major, medium and minor peaks at the electron kinetic energies of 502.5, 485 and 465 eV, which are assigned to $(\mathrm{O}{:}2p)^{-2}(4a_1 \text{ (or } 2b_2))^1$, $(\mathrm{O}{:}2s)^{-1}(\mathrm{O}{:}2p)^{-1}(4a_1 \text{ (or } 2b_2))^1$, and $(\mathrm{O}{:}2s)^{-2}(4a_1 \text{ (or } 2b_2))^1$ spectator Auger final states, respectively. These results shows that ultrafast ion desorption (UFID) mechanism is predominant at the $4a_1$ and $2b_2$ resonances. The enhancement of the H^+ AEPICO yield was attributed to the strongly O-H antibonding character of $4a_1$ and $2b_2$ orbitals. At the 3*p* resonance ($h\nu$ = 535.4 eV), the AEPICO yield spectrum exhibited major, medium and minor peaks at the electron kinetic energies of 460, 475 and 490 eV, which are assigned to $(2a_1)^{-2}(3p)^1$, $(2a^1)^{-1}(1b_2)^{-1}(3p)^1$, and $(1b_2)^{-2}(3p)^1$ spectator Auger final states, respectively. This result indicates that spectator Auger stimulated ion desorption (SASID) mechanism is responsible at the 3*p* resonance. The suppression of the H^+ AEPICO yield was attributed to the reduction of the hole-hole Coulomb repulsion due to the 3*p* electron. At $h\nu$ = 540.6, 547.6 and 557.8 eV, the AEPICO yield spectrum exhibited three peaks at the electron kinetic energy of 460, 475 and 490 eV, which are assigned to $(2a_1)^{-2}$, $(2a_1)^{-1}(1b_2)^{-1}$, and $(1b_2)^{-2}$ normal Auger final states, respectively. This result indicates that the normal Auger stimulated ion desorption mechanism is responsible at photon energies above the O:1*s* ionization. These results and conclusions are consistent with the previous study carried out by low-resolution AEPICO spectroscopy.[1)]

Reference
1) K. Mase, *et al.*, *J. Chem. Phys.* **108**, 6550 (1998).