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Synchrotron-radiation-stimulated etching of SiO_2 thin films with a tungsten nano-pillar mask

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A nano-pattern of SiO_2 on a Si (100) surface has been demonstrated by synchrotron-radiation-stimulated etching with a tungsten nano-pillar mask. The reaction gas was a mixture of SF_6 and O_2. The mask was fabricated using a focused ion beam with $W(CO)_6$ as the source gas. The width and height of the tungsten nano-pillar were ~80 nm and 160 nm, respectively. Synchrotron radiation irradiation with flowing SF_6 and O_2 effectively etches the silicon dioxide, and the etching process followed the surface photochemical reaction. The etched surface was very flat, and no undercutting occurred during the etching process.

Keywords: synchrotron-radiation-stimulated etching; tungsten nano-pillar mask; SiO_2 thin films; surface photochemical reaction; etched pattern.

1. Introduction

Fine patterning techniques in etching have been in great demand in micro-fabrication. Ultra-large-scale integrated circuits have been developed extensively over the past tens of years, and the size of one element has been very much reduced. However, it is difficult to integrate further using conventional processes, and thus a new process has been desired in microelectronics manufacturing. Strong soft X-rays from an undulator in a storage ring are expected to solve this requirement (Ogawa *et al.*, 1994). Synchrotron radiation should be an ideal light source for the study of photochemical reactions owing to various characteristics in the soft X-ray region, such as high intensity, continuity of wavelength and small divergence. Most gas molecules and solids used in semiconductor processes have a large cross section in the soft X-ray region and can be electronically excited at the core or valence levels by synchrotron radiation. Synchrotron-radiation-stimulated etching has attracted considerable attention from the viewpoint of developing new surface micromachining technologies owing to its unique features of high spatial resolution, extremely high material selectivity, anisotropy etching, low damage and clean etching atmosphere (Urisu & Kyuragi, 1987; Takahashi *et al.*, 1991). In preceding works synchrotron-radiation-stimulated etching of SiO_2 thin films was conducted using a contact cobalt mask, and a micro-pattern of SiO_2 thin films was made for the area-selective deposition of self-assembled monolayers (Wang & Urisu, 2003). The cobalt contact mask on the SiO_2 surface was fabricated by sputtering Co thin film on a photolithography resist pattern and using a lift-off technique. In this paper, synchrotron radiation etching of the SiO_2/Si surface has been examined using a tungsten nano-pillar mask to manufacture a nano-pattern of SiO_2 thin films on the silicon substrate. The tungsten mask was deposited on the SiO_2 surface by a focused ion beam with $W(CO)_6$ source gas.

2. Experiment

Fig. 1 shows the schematic process of sample preparation and synchrotron-radiation-stimulated etching. A single-crystal silicon wafer was cut and thoroughly cleaned with acetone, ethanol, deionized water and a solution of concentrated H_2SO_4 and H_2O_2. The cleaned wafer was immersed in a dilute HF solution for 2 min to remove its native oxide. The SiO_2 thin film was formed on the freshly cleaned Si surface by annealing at 1173 K for 10 h in a dry oxygen atmosphere. The thickness of the SiO_2 film measured with an ellipsometer was about 220 ± 10 nm. On the SiO_2 surface, a W pillar mask was fabricated using focused ion-beam-induced chemical vapor deposition (FIB-CVD) (SII NanoTechnology) with Ga ions and $W(CO)_6$ source gas. FIB-CVD is a common technique of direct patterning of metallic or insulator films used for

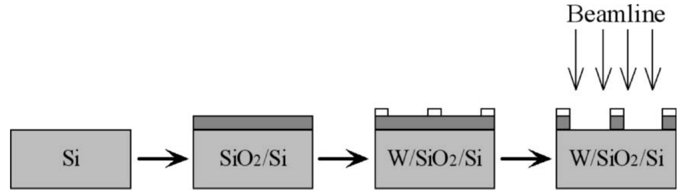

Figure 1
Schematic process of the sample preparation and synchrotron-radiation-stimulated etching.

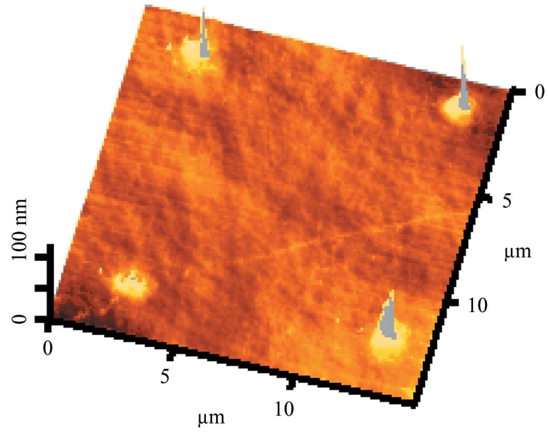

Figure 2
AFM quasi-three-dimensional image of the tungsten nano-pillar.

repairing electronic devices and photomasks. The method of using FIB-CVD with $W(CO)_6$ source gas to deposit three-dimensional tungsten structures has already been reported (Koops *et al.*, 1988). The W pillar mask was deposited with a gas pressure, acceleration voltage and ion current of 1×10^{-3} Pa, 30 kV and 0.5 pA, respectively, and the deposited pillar usually contains tungsten, carbon, oxygen and gallium (Ishida *et al.*, 2003). A portion of the tungsten mask on the SiO_2 surface is shown in Fig. 2. The transverse width and longitudinal height of the tungsten pillar were ~80 nm and 160 nm, respectively.

Synchrotron radiation etching of SiO_2/Si (100) substrate was conducted using a mixture of SF_6 and O_2 as the reaction gas at beamline 4A2 of the synchrotron radiation facility (UVSOR) at the Institute for Molecular Science of Japan. A large pressure difference between the etching chamber and the beamline was sustained by using a differential vacuum pumping system. The sample was set normal to the incident synchrotron radiation beam. Synchrotron radiation light irradiated the sample surface directly; no window was used. Details of the apparatus for synchrotron radiation etching have been described in an earlier paper (Hirano *et al.*, 1998). The beam diameter on the sample surface was ~9 mm and the beam current of the storage ring was ~200 mA.

3. Results and discussion

In the experiment, SiO_2 was found to be effectively etched by synchrotron radiation with SF_6 + O_2 as the reaction gas at room temperature. The etching took place only in the area irradiated with synchrotron radiation and proceeding in the direction of the incident beam, as shown in Fig. 3. In this figure the SiO_2 thin film on the silicon substrate was directly irradiated with synchrotron radiation in an atmosphere of SF_6 + O_2 gas mixture without a mask. No noticeable etching of SiO_2 was found when SF_6 was not put in the etching chamber, the sample substrate was only exposed to synchrotron radiation at room temperature. It has been reported that an amorphous SiO_2 (α-SiO_2) film continuously decomposes and evaporates when irradiated with synchrotron radiation at elevated substrate temperatures (Akazawa, 1995). Why do we call it synchrotron-radiation-stimulated etching? There are two main types of reaction mechanism in photo-excited etching at room temperature (Urisu & Kyuragi, 1987; Kitamura *et al.*, 1994). One is a gas-phase photochemical reaction in which photo-excitation of the surface does not take part in the reaction and the etching reaction occurs spontaneously. The other is a surface photochemical reaction in which photo-irradiation of the surface is necessary for the etching reaction. This experimental result suggested that photo-excitation of material surfaces and the following chemical reactions played important roles in synchrotron-radiation-stimulated etching. Under the irradiation of synchrotron radiation, the SiO_2 molecule was excited by high-energy photons to a reactive or excited state, and SF_6 molecules produced F ions. The excited SiO_2 reacted with the F ions, and then the resulting compounds decomposed and evaporated. Therefore, the surface excitation was dominant in the above synchrotron-radiation-exited etching SiO_2/Si system. Anisotropy etching was achieved owing to a surface photochemical reaction. This property is practical for fabricating extremely fine patterns with a high aspect ratio.

In our previous publication (Wang & Urisu, 2003) it was reported that the etching rate depended on the surface intensity of the synchrotron radiation beam and the surface density of the reaction molecules. It increased with increasing SF_6 gas pressure in the range where the attenuation of the beam intensity due to gas absorption was negligible. In the region of higher gas pressure the beam intensity was attenuated by the reaction gas absorption and the etching rate saturated or decreased. In addition, the etching rate increased with decreasing substrate temperature. Thus, the etching rate can be increased by optimizing the reaction gas pressure and by decreasing the substrate temperature. Furthermore, the etching process stopped completely on the SiO_2/Si interface if a little O_2 was added to the reaction gas. The synchrotron radiation irradiation with flowing SF_6 + O_2 did not etch the silicon crystal, *i.e.* high etching selectivity can be obtained between Si and SiO_2 layers. Based on these experiments, we carried out the synchrotron-radiation-stimulated etching of

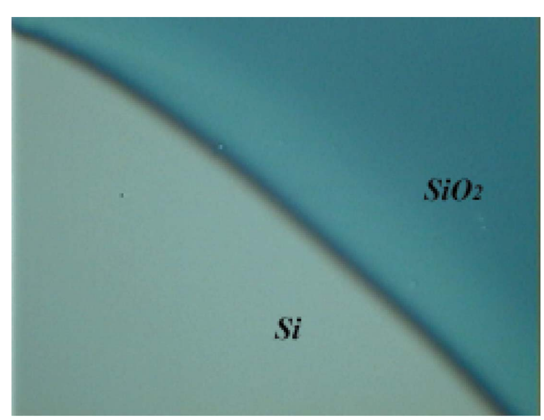

Figure 3
CCD image of a portion of the synchrotron-radiation-etched structure without a mask.

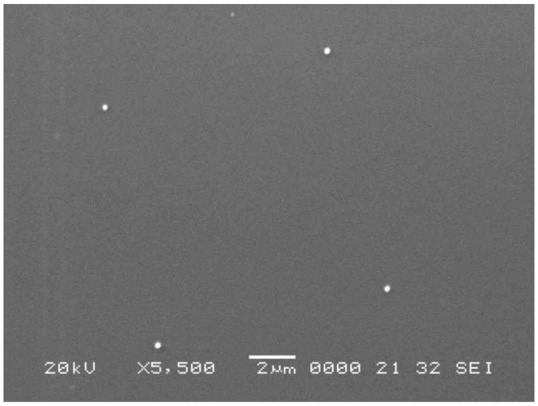

Figure 4
SEM image of the synchrotron-radiation-etched pattern with a tungsten pillar mask.

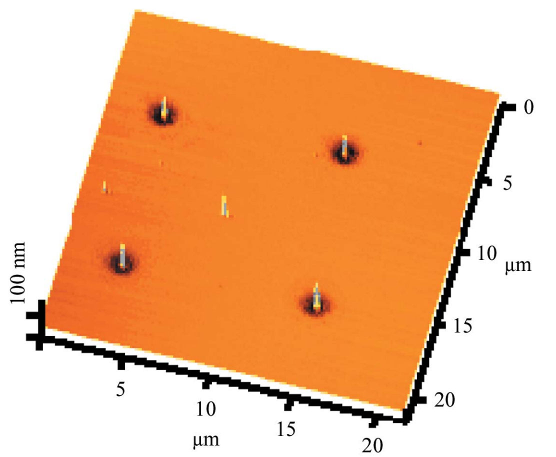

Figure 5
AFM quasi-three-dimensional image of the synchrotron-radiation-etched pattern with a tungsten pillar mask.

SiO_2 thin films with a tungsten mask. The synchrotron-radiation-etched pattern with tungsten masks was observed using a scanning electron microscope (SEM) (Jeol, JSM-5510) and an atomic force microscope (AFM) (SII, SPI3800N/SPA400) in dynamic force mode with a 20 μm scanner and a SI-DF40 (spring constant = 42 N m^{-1}) cantilever. Figs. 4 and 5 show the SEM and AFM images of the synchrotron-radiation-etched pattern with tungsten pillar masks, respectively. Patterning SiO_2 thin film on the silicon surface in the nano-scale was achieved by synchrotron-radiation-stimulated etching. In the etching experiment the irradiation dose of the synchrotron radiation beam was about 10000 mA min and the gas pressure of SF_6 and O_2 was about 0.05 torr and 0.002 torr, respectively. From these images it can be concluded that no undercutting had occurred, and the unique features of synchrotron-radiation-stimulated etching such as high spatial resolution, high material selectivity and anisotropy etching are proven. Moreover, the synchrotron-radiation-etched surface looked very flat and uniform, which is important when utilizing this pattern template (Wang & Urisu, 2003; More *et al.*, 2002). Similar characteristics were reported in another paper in which the roughness with a line profile on the synchrotron-radiation-etched surface was 0.05 nm. The maximum difference in height in the observed surface was less than 0.2 nm and the sloping angle between two positions in the observed surface was less than 1.2° (Wang & Urisu, 2005). The hollow appearing around the tungsten pillar was perhaps due to damage of the silicon crystal during fabrication of the tungsten mask. The damaged silicon was likely etched by synchrotron radiation irradiation with flowing SF_6 + O_2 mixture gas. The exact mechanism of this phenomenon is not yet clear. Further investigations are in progress.

4. Conclusion

Based on previous synchrotron-radiation-stimulated etching, a SiO_2 nano-pattern structure has been fabricated onto a silicon surface using SF_6 + O_2 as the reaction gas and a tungsten nano-pillar mask. Etching of SiO_2 occurred due to a surface excitation reaction which involved the interaction between the excited states of the Si–O bond and F ions or radicals. A high spatial resolution and anisotropy etching was displayed, and the etched surface was very flat. Synchrotron-radiation-etched patterns will be an interesting structure for many kinds of silicon-based devices (Miqin *et al.*, 1998).

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