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Direct Pattern Delineation of Fluoride Films with Multilayer-Monochromatized Synchrotron Radiation with Real-Time Monitoring by SR-Excited Auger Electrons

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Direct pattern delineation of fluoride films is achieved through the use of strong synchrotron radiation semi-monochromatized by applying a multilayer. Etching processes of CaF_2 and SrF_2 are found to be very sensitive to substrate temperature. Simultaneously monitored SR-excited Auger electron spectra reveal that fluorine atoms are selectively desorbed from SR-irradiated surfaces at low temperature, and are desorbed stoichiometrically with Ca atoms at 400 °C.

1. Introduction

Direct pattern formation techniques are becoming increasingly important in semiconductor device fabrication, because they have a possibility of reducing process steps. Recently Akazawa et al[1] reported the synchrotron radiation(SR) direct etching of SiO_2 without using etching gases. However, the etching or evaporation rate of SiO_2 was rather small such as less than 10Å/100mA/min even at 600° C substrate temperature.

In the fabrication process of GaAs MIS devices, CaF_2 and SrF_2 films are used for epitaxial gate insulator[2], which exhibits a very low density of interfacial states. Since these fluoride films cannot be selectively delineated by means of reactive ion etching, probably because they previously contain fluorine atoms, Ar ion etching followed by chemical etching was utilized for device fabrication. Therefore, direct pattern formation with SR may drastically reduce these complicated steps.

In this study, a new technique for pattern delineation though the use of strong synchrotron radiation semi-monochromatized by applying a multilayer is investigated to facilitate the selective etching of fluorides on GaAs and Si substrates. The semi-monochromatic beam energy was set at about 1000 eV in order to use transparent X-ray masks on SiN membrane.

Surface compositions and chemical states were simultaneously monitored during SR etching by means of SR-excited Auger electron spectroscopy.

2. Experiments

Experiments were performed at Beamline 1A of the Photon Factory in the National Laboratory for High Energy Physics. This beamline consists of a paraboloidal front-mirror for collimating 4 mrad beam horizontally, a grating/crystal monochromator [3] with a first crystal and a second crystal, and a paraboloidal rear-mirror for focusing the beam at 38.5 m from the SR source point. The divergence of the focusing beam was about 5 mrad.

A W/B_4C multilayer of 123Å d-spacing, which was formed on a 3" SiC substrate with a dual RF-sputtering gun apparatus[4], was installed in the first crystal holder of the grating/crystal monochromator. The monochromatized output by applying this multilayer was characterized by a 2400g/mm grating installed in the second crystal holder. Figure 1 shows photon flux as a function of photon energy. Here, the grazing incidence angle (α) to the multilayer and the grating was set at 86 ° to obtain the maximum photon flux at about 1000 eV. It was found that the output included the reflected light component as well as the diffracted light component which has a peak at 1000 eV of $h\nu$.

Samples were CaF_2 and SrF_2 films evaporated on Si(100) substrates at room temperature in UHV from tungsten baskets. X-ray diffraction experiments indidcated that these films were not crystalized. The semi-monochromatic SR beam was irradiated onto the samples which were heated. Temperature was measured with an IR thermo-spot sensor. During the etching processes, Auger

electrons excited by the same semi-monochromatic SR beam as the etching source beam were analyzed with a CLAM analyzer.

3. Results and discussion

3.1 Etching properties of CaF_2 and SrF_2

When CaF_2 and SrF_2 films were irradiated at room temperature with the multilayer-monochromatized beam, the irradiated area was not etched off. However, it was found that these films are etched-off at elevated temperatures. Figure 2 shows etching rates of CaF_2 and SrF_2 films at various substrate temperatures. The CaF_2 film was only slightly etched off at 300°C, and something like white residue was left on the SR-irradiated surface. As will be shown later, it was metallic Ca formed after SR-stimulated F desorption. However, when the substrate temperature was maintained at 400°C, a practical CaF_2 etching rate of about 70 Å/min was obtained without any selective desorption of fluorine. At 500°C and higher, the etching rate decreased down to about 40 Å/min, and the irradiated surface became rough, implying that the size of polycrystals became larger and the grain boundary might be selectively etched. This result is quite opposite to the results for photostimulated evaporation[1] of amorphous SiO_2 where the etching rate increases monotonically with increasing the substrate temperature. Although the cause of this difference is not clear at the present stage, it may be attributed to crystallization process of CaF_2 at about 500°C which caused the evaporation rate of CaF_2 to decrease. Since CaF_2 and SrF_2 films are not etched only by heating without SR irradiation, these etching processes are regarded as SR-enhanced evaporation.

On the other hand, the SrF_2 films showed slightly different features from the CaF_2 case. The etching rate increases up to 500 °C, which is similar to the SiO_2 case. Since the Ca-F bond strength of 125 Kcal/mole is almost the same as the Sr-F bond strength of 125.6 Kcal/mole, the different etching features cannot be attributed to bond strength difference between Ca-F and Sr-F. Then, we thought of the surface reactions such as

$$SrF_2 \Rightarrow SrF + F \quad (1)$$
$$SrF \Rightarrow Sr + F \quad (2).$$

Although we have no data about SrF and CaF to our knowledge, we can compare the vapor pressure of Ca and Sr metals. Actually, the vapor pressures of Ca and Sr, respectively are about 1×10^{-5} Torr and 1×10^{-4} Torr at 400°C. In other words, when the SR beam caused decomposition and F desorption at 400 °C, the probability that Ca metal will remain at the surface is one order of magnitude higher than that for the Sr case. Therefore, Sr and F co-evaporation may take place. Thus, SrF_2 is regarded as more suitable for the SR-enhanced etching than CaF_2.

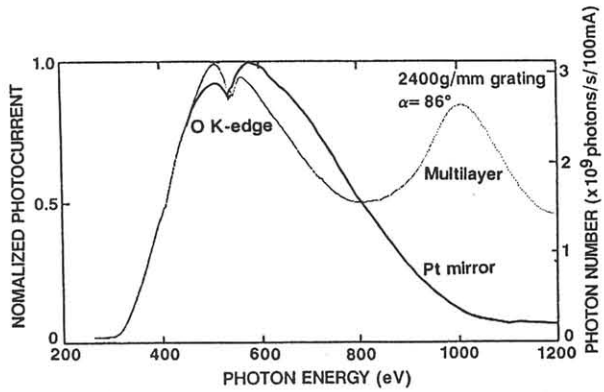

Fig. 1 Monochromatization characteristics obtained by applying a multilayer or a Pt mirror as the first optical element in the grating/crystal monochromator. The incidence angle of synchrotron radiation to the multilayer and the grating was 86 ° .

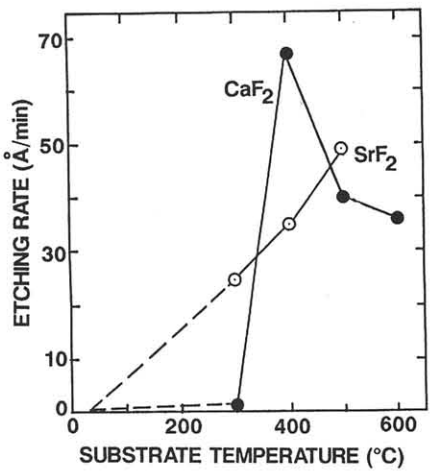

Fig. 2 Synchrotron radiation etching properties as a function of substrate temperature. Samples are CaF_2 and SrF_2 films deposited on Si(111) substrates at room temperature.

3.2 Real-time Auger electron spectroscopy

In order to investigate what happens at the surface during SR etching, SR-excited Auger electrons were measured in situ with the CLAM analyzer. Since the primary probe for Auger excitation was the SR beam itself for etching, this was indeed a real-time analysis. On the fresh CaF_2 surface, Ca $_{LVV}$ Auger peak in the CaF_2 state and F $_{KLL}$ peak were clearly observed. On the contrary, for the 45 min-irradiated surface, Ca $_{LVV}$ peak shifted towards higher kinetic energy and its shape drastically changed, suggesting

that the Ca atoms are in the metallic Ca state. This is also confirmed by the fact that F $_{KLL}$ Auger peak disappeared on the surface. Thus, the very small etching rate of CaF_2 at 300 °C can be attributed to the strong F desorption and the Ca metallic overlayer which may act as a prohibitor of further etching. This phenomenon resembles the case where Si substrates are hardly etched by reactive ion etching in a reduction atmosphere involving CF_4 + C_2H_4 gases; here, carbon residue on the Si surface plays the roll of eliminator of fresh Si atom sites, resulting in the rather high etching selectivity of SiO_2 to Si[5] .

3.3 Direct pattern delineation

Next, the SR irradiation etching technique was applied to direct pattern delineation process of CaF_2 films. A #2000 mesh was used as a mask and placed less than 1mm above the CaF_2 sample. As shown in Fig. 3, a clear mesh image was formed, when the CaF_2 substrate temperature was kept at 400 ° C. However, the etched surface was rather rough at 500° C substrate temperature. And, almost no pattern was obtained at 300 °C.

The etching process was monitored by F $_{KLL}$ Auger electrons which were ejected from the surface through the mesh pattern window. Figure 4 shows F $_{KLL}$ Auger peak intensity change during SR irradiation. At 400 °C of substrate temperature, CaF_2 shows F desorption only slightly. However, a large amount of F desorption takes place at 500 °C, which might be the reason for the rough etched surface.

Although a clear fine pattern is not formed with the transparent X-ray mask at the present stage, this technique has a good potential for device fabrication applications, because the SR beam does not etch Si or GaAs substrates at all, and many resist processes can be eliminated.

4. Conclusion

We developed a novel technique for pattern delineation of fluoride films through the use of strong synchrotron radiation semi-monochromatized by applying a multilayer. The etching rates of CaF_2 and SrF_2 are found to strongly depend on substrate temperature, which might be due to vapor pressures of residual metals and the crystallization effect of fluorides. Furthermore, the etching process could be simultaneously monitored by SR-excited Auger electron spectroscopy, which reveals that fluorine atoms are selectively desorbed from SR-irradiated surfaces at low temperature, and that Ca and F atoms are desorbed stoichiometrically at 400 °C.

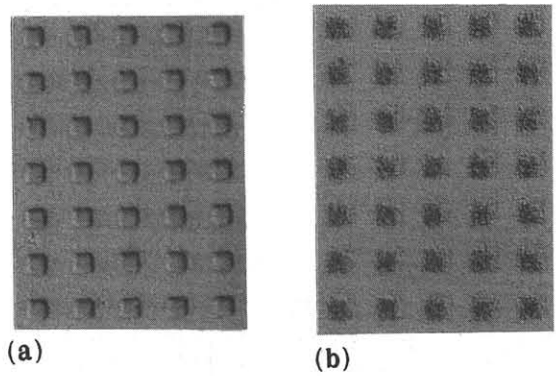

Fig. 3 SR-etched mesh patterns on CaF_2/Si at (a) 400℃ and (b) 500℃ for 50 min. A #2000 mesh was placed less than 1 mm above the CaF_2 films. The etched area is about 6 μm x 6 μm .

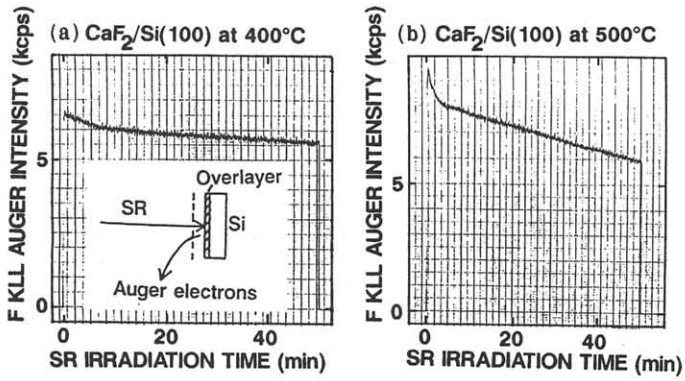

Fig. 4 Simultaneously-monitored F $_{KLL}$ Auger signal intensity as a function of SR irradiation time at 400°C (a) and 500°C (b). Samples are CaF_2 films.

References

1) H. Akazawa, Y. Utsumi, J. Takahashi and T. Urisu, Appl. Phys. Lett., 57 (1990) 2302.

2) T. Waho and H. Saeki, Jpn. J. Appl. Phys., 30 (1991) 221.

3) T. Kawamura, S. Maeyama, M. Oshima, Y. Ishii and T. Miyahara, Rev. Sci. Instrum., 60 (1989) 1928.

4) H. Takenaka, H. Kinoshita, K. Kurihara, T. Mizota, T. Haga, S. Maeyama, M. Oshima and Y. Ishii, Photon Factory Activity Report 1990, p. 33.

5) S. Matsuo and M. Takehara, Jpn. J. Appl. Phys., 16 (1977) 175.