FINE PATTERN ETCHING OF SILICON USING SR-ASSISTED IONIZATION OF CF₄ GAS

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A new etching method of semiconductor materials using ionization of CF₄ gas by synchrotron radiation (SR) and acceleration of SR-generated ions by external electric field is proposed. The SR is irradiated parallel to the substrate and the electric field is applied perpendicular to the substrate. The dominant quasi-stable gas-phase ion is CF₃⁺ which is measured by photo-ionization mass analysis. This method is applied to etch silicon substrate having resist mask and fine pattern of 0.1μm line and space is successfully fabricated.

1. Introduction

Photoexcited reactions for semiconductor device manufacturing have been widely studied using lasers and discharge lamps as light sources.[1,2] The low-temperature and low-damage processes realized by photoexcitation have great potential for fabricating fine-structured microelectronic devices in the future. However, the photon energies of these conventional light sources are often insufficient to dissociate the bonds of source materials in a single photon process.

Synchrotron radiation (SR) is a promising light source for photoexcitation because the soft X-ray to vacuum ultraviolet light provided by SR can efficiently decompose the source gas used in the process. Several experiments have been demonstrated for SR-excited etching of semiconductor materials, such as carbon film, polysilicon, Si, SiO₂, SiC, and refractory metals.[3-9] In all of these experiments, SR was used perpendicular to the substrate. Although the perpendicular irradiation may be effective in exciting the surface adsorbed molecules and/or the substrate itself, the following disadvantages seem to occur. (1) With perpendicular irradiation, a uniform and large-area etching is impossible because the SR cross section is usually limited to the cross section of the slits (usually less than 10x10mm) in the differential pumping system. A differential pumping system is necessary to maintain the pressure difference between the ultrahigh-vacuum beam line and the low-pressure reaction chamber during deposition or etching. (2) For a practical application, resist film is used as an etching mask. Ablation reaction induced by direct SR irradiation will break the bonds in the resist molecules and as a result, the resist is evaporated. This phenomena inhibits the use of the resist material.

One way of overcoming these problems is SR irradiation parallel to the substrate. By parallel SR irradiation, the substrate surface is uniformly exposed to photogenerated radicals, making the processed area larger than that of perpendicular irradiation. Ablation of resist material is also avoided

by parallel irradiation. By irradiating SR to the reaction gas, ionized species are generated because the photon energy of SR is usually larger than the ionization potential of the source gas. These ions can be accelerated when the external electric field is applied. Moreover, in this method, the generation of gas phase ions and acceleration of generated ions are completely separated. Therefore, it is expected that this etching process has superior controllability over the conventional reactive ion etching method, in which the ions are generated and accelerated simultaneously by the applied RF voltage.

In this paper, we will propose a new etching method of semiconductor materials by accelerating SR-generated ions to the substrate. We will show the experimental results about ionization process of tetrafluoromethane (CF_4) gas observed by mass analysis and line and space pattern fabrication having a dimension of $0.1\mu\text{m}$.

2. Experimental setup

Experiments were performed using the SR beam line BL-17B at the Photon Factory at the National Laboratory for High Energy Physics.[10] With this beam line, SR from a 2.5GeV storage ring was reflected and focused by a toroidal mirror 12m from the source point. The SR beam is introduced at an etching chamber placed about 29m from the source point. Differential pumping system was installed between the beam line and etching chamber in order to maintain the pressure difference.

Figure 1 shows the power spectrum of the SR. The absorption and ionization cross section values CF_4 gas given by Zhang et al.[11] are also shown in the figure. The available photon energy at the etching chamber was approximately less than 1000eV, which was determined by the incidence angle of the toroidal mirror (5°). The total photon intensity was estimated to be about 10^{16} photons $\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$. The photo absorption of CF_4 gas begins at the photon energy around 12eV and takes a maximum value at about 22eV. The ionization of CF_4 molecule begins at the first ionization energy at 16.2eV. When the photon energy is more than 20eV, absorption and ionization cross section take almost same values. This means that the fluorocarbon ions are efficiently produced by SR irradiation.

The photo generated gas-phase ions were detected by using the photoionization quadrupole mass analyzer (ULVAC MSQ-400). In this measurement, the filament of the mass analyzer was switched off and only the photogenerated positive ions were detected. The pressure of the CF_4 gas was changed from 1×10^{-8} to 1×10^{-6} Torr during the measurement. The mass number was scanned from $m/e=1$ to 90 to detect the fluorocarbon ions in the gas phase.

For the pattern fabrication experiments, resist (CMS) patterns were fabricated on Si(100) n-type substrate by using electron beam exposure. The minimum pattern size was $0.1\mu\text{m}$ lines and spaces. Resist thickness was $0.1\mu\text{m}$.

Figure 2 shows the apparatus around the etching chamber. The etching chamber was evacuated by turbomolecular pump to a base pressure on the order of 10^{-7} Torr. The SR is introduced to the etching chamber through slits of differential pumping system. The cross section of SR is defined by

the last slit of the differential pumping system, having a size of 1mm vertical and 10mm horizontal. At the center of the etching chamber, a pair of electrodes was set. The distance of the two electrodes were 5mm. The sample substrate was set on the lower electrode. Both electrodes were electrically isolated from the chamber wall. The upper electrode was connected to the ground potential and the lower electrode was connected to the voltage source to apply an electric field between electrodes. SR was irradiated parallel to the substrate at the center of the electrodes. CF_4 gas was introduced to the etching chamber through a variable leak valve to a pressure up to 0.05Torr.

Fig. 1. Power spectrum of the beam line and the absorption and ionization cross section of CF_4 gas.

Fig. 2. Experimental apparatus around the etching chamber.

3. Results and Discussion

Mass spectrum measurement

We first examined the gas phase dissociation and ionization of CF_4 gas by SR irradiation because, in the etching method described above, gas phase ions are utilized in etching process. Figure 3 shows the mass spectrum of CF_4 gas irradiated by SR. The partial pressure of the CF_4 gas was kept at 1×10^{-6} Torr.

Fig. 3. SR-ionized mass spectrum of CF_4 .

In the mass spectrum, photo-ionized ions such as CF_3^+ , CF_2^+ , CF_2^{2+} , CF_3^{2+} , CF^+ , F^+ , and C^+ are observed. The major ion was CF_3^+ whose intensity was more than ten times larger than other ions. The intensities of these ions were proportional to the CF_4 pressure, showing these ions were produced through direct ionization by SR irradiation. Zhang et al. [11] measured photo ionization of CF_4 gas using time of flight method. They observed photo ionization at the photon energy larger than 20eV and obtained the almost the same branching ratios of ions as our results at the photon energy of 40-50eV. However, the amount of doubly charged ions is larger in our case. This is probably because the SR is white light including photon energy up to about 1000eV and the effect of core electron excitation of C and F atoms appeared.

SR generated ion current

Ion current between the two electrode was measured as a function of the applied DC voltage. Figure 4 shows the results. The CF_4 pressure was varied from 10^{-5} to 10^{-2} Torr. Negative DC voltage (from 0 to -400V) was applied to the lower electrode. The potential of the upper electrode was kept 0V. SR was irradiated at the center of the two electrodes parallel to the electrodes. Ion current was normalized at the storage ring current of 300mA. The ion current increased by increasing the negative applied voltage and showed almost constant value at the DC bias below -50V. This means that almost all the photo-generated ions between the electrodes could be collected in the lower electrode at the DC bias below -50V. Without SR irradiation, no ion was generated in the gas phase and the ion current was in a level of detection limit (several pA) of the system. Figure 5 shows the relation between ion current and CF_4 pressure at the substrate bias of -100V. When the CF_4 pressure was more than 10^{-5} Torr, the ion current almost linearly increased with the CF_4 pressure. At the CF_4 pressure of 0.05Torr, the ion current of more than 10^{-4} A was obtained with this method. From these experimental results, it is shown that CF_4 gas is ionized by SR irradiation and ions, whose number is almost proportional to the gas phase CF_4 molecules, are accelerated to the substrate surface.

Fig. 4. Ion current between the two electrodes as a function of applied DC bias and CF_4 pressure.

Fig. 5. CF_4 pressure dependence of the ion current. The applied bias was kept at -100V.

Silicon etching characteristics

Etching experiment was performed with placing a silicon substrate having resist mask on a lower electrode and applying a negative DC bias to the substrate. Figure 6 shows the relation between the etching depth and CF_4 pressure. The SR exposure was $1000\text{A}\cdot\text{s}$ and substrate DC bias was -200V . The etching depth linearly increased with the increase of CF_4 pressure. This tendency is the same as the impinging ion density to the substrate surface. When increasing the substrate DC bias, the etching depth slightly increased. It is thought that the physical sputtering phenomenon may also included in the etching reaction.

Fig. 6. Silicon etched depth as a function of CF_4 pressure.
SR exposure was $1000\text{A}\cdot\text{s}$. Substrate DC bias was kept at -200V .

Figure 7 shows the SEM photograph of the etched silicon surface when the photo-generated ion was accelerated by DC voltage. Pattern was $0.4\mu\text{m}$ lines and spaces. The cross sectional structure of the etched surface had the "tapered" shape. This shows that the fine pattern etching of $0.1\mu\text{m}$ level was impossible by using this method. This is probably due to the "charge built-up" effect of the resist surface by impinging ions. To avoid the "charge built-up" effect, we accelerated the photo-generated ions by AC voltage. Positive (photo-generated ions) and negative (photo electrons) particles are alternately accelerated by AC voltage and surface charge may be effectively neutralized. As a result, an improvement of etched pattern shape is expected. Figure 8 shows the SEM photograph of the silicon surface etched by AC acceleration voltage (AC 150V) with CF_4 pressure of 0.05Torr . The amplitude and frequency of applied AC voltage was 150V (rms value) and 100Hz , respectively. It can be seen that the "charge built-up" effect was effectively suppressed and fine structure of $0.1\mu\text{m}$ line and space was accurately transferred to the silicon surface. The etching rate increased almost linearly with the increase of the amplitude of the AC voltage in the range from 50 to 200V . The etching rate was almost constant when the frequency was changed from 50 to 1000Hz . This is due to the fact that the flight time of the CF_3^+ ion between the two electrode is estimated about $0.2\mu\text{s}$ when the applied bias is 250V and the applied AC period is slow enough compared with the flight time.

Fig. 7. SEM photograph of silicon surface etched by DC acceleration voltage. Pattern is 0.4 μ m lines and spaces.

Fig. 8. SEM photograph of silicon surface etched by AC acceleration voltage. Pattern is 0.1 μ m lines and spaces.

4. Conclusions

We proposed a new etching method, in which SR is irradiated parallel to the substrate and SR-excited gas-phase ions are accelerated to the substrate by applied electric field. In this method, the processed area becomes larger compared with the conventional perpendicular irradiation and the ablation of resist material is also avoided. We presented here preliminary experimental results using the proposed method.

When using the SR light having the energy range from 1 to 1000eV and CF₄ gas as an etching gas, the dominant gas-phase ion was CF₃⁺ and ion current impinging to the substrate was more than exceeding 10⁻⁴A. Silicon etching rate almost linearly increased with the CF₄ pressure and accelerating voltage. When the SR-excited ions were accelerated by DC voltage, the cross sectional structure of the etched surface had the "tapered" shape, due to the "charge built-up" effect of the resist surface by impinging ions. Accelerating ions by AC voltage could effectively suppressed the "charge built-up" effect and fine pattern of 0.1 μ m line and space was accurately transferred to the silicon surface.

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