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Laser induced fluorescence monitoring of the etching processes with the inward plasma

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ABSTRACT

Laser induced fluorescence (LIF) spectroscopy has been used to monitor the etching processes in a localized plasma etching system. An inward plasma was employed for etching in which etching gas was discharged in the narrow gap between the etched sample and the entrance of an evacuating capillary tube. By observing the LIF spectrum, it was confirmed that the etch product SiF_2 exists near the both Si and SiO_2 sample surfaces being etched with CF_4 inward plasma. The plasma gas temperature was estimated to be ~400 K from the comparison of the LIF spectrum with the rotational simulation. LIF method was applied to the etching endpoint detection of two kinds of material, thermally-grown SiO_2 on Si and spin-coated Polyimide Isoindoro Quinazorindione (PIQ) film on Si. The endpoint was detected from the onset of SiF_2 production by the etching of Si substrate in the case of PIQ/Si. The signal intensity of SiF_2 from the Si substrate during etching was several times larger than that from the SiO_2 layer, and thus, the endpoint of SiO_2 etching was detected by the abrupt increase of SiF_2 signal. The etch rates of PIQ and SiO_2 at the center of the capillary were determined to be 1.09 μm/min and 1.66 μm/min, respectively.

1. Introduction

Plasma has been widely used for dry etching and surface functionalization of various materials such as semiconductors, metals, dielectric and organic materials, and respective thin membranes. We have recently developed a localized plasma etching apparatus using a novel phenomenon which we denominate “inward plasma” [1]. The etching chamber is filled with an etching gas and evacuated through a capillary tube (inner diameter 0.5 mm−5 mm) whose entrance is close (<500 μm) to the sample surface. An electric field of a radio frequency (13.56 MHz) is applied to an electrode surrounding the capillary tube to generate the plasma in the capillary. Part of generated plasma goes upstream against the etching gas flow [2] and is localized in the narrow gap between the sample and the entrance of the capillary. The inward plasma etching technique has several advantages. When CF_4 is used as the etching gas, high etch rate (>10 μmSi/min) can be achieved with low power (<50 W). Damage of the sample caused by the temperature rise is reduced since fresh cool gas is continuously supplied to the sample surface. Etching products are immediately evacuated through the capillary and no debris is left on the sample surface. Owing to the localized nature of the inward plasma within the diameter of the capillary tube, direct patterning is possible by scanning the sample with the capillary entrance, etc.

The apparatus was originally developed for failure analyses in semiconductor electronic devices. Failure analyses in the research and development stage have become more important as progress in semiconductor devices is being accelerated [3]. To find the cause of failure in devices, it is necessary to expose the metal lines embedded in insulators in the device locally and effectively without any damage to the circuit. The features of the inward plasma mentioned above are especially suitable for this purpose. It is demonstrated that the developed apparatus effectively etches the insulation layers of large-scale integrations (LSI) devices to expose the metal lines with no damage and without leaving debris. This new etching technique with inward plasma has significantly reduced time and cost used for pretreatments compared with the conventional method of combination of chemical mechanical

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polishing (CMP) and focused ion beam (FIB).

Monitoring of plasma status is also important to optimize and maintain the etching processes. By taking another advantage of the inward plasma system, i.e., effective collection of the etching products through the capillary, Takahashi et al. monitored the gas ingredients using quadrupole mass spectrometry (QMS) at the exit of the capillary [4]. In addition to signals stemming from the CF_4 gas, mass signal peaks at m/z = 47, 66 and 85 corresponding to SiF^+, SiF_2^+ and SiF_3^+ species, respectively, were observed in the etching of Si and SiO_2 with CF_4 plasma. These ionic species were considered to be generated by the cracking of the neutral parent etching product SiF_4 by the electron impact ionization at 70 eV [5]. When monitoring the signal intensity of m/z = 85 while etching SiO_2/Si sample, the signal intensity increases abruptly at certain etch time, which indicates that the SiO_2 layer was etched completely and Si substrate was exposed. The mass peaks at m/z = 47 and 66, however, did not show significant intensity change, which led the authors to conclusion that these signals may not be SiF^+ and SiF_2^+, but COF^+ and COF_2^+, respectively.

In addition to fragmentation caused by cracking of larger mass species due to electron impact ionization and interference from species having the same mass number, mass spectrometry have difficulty in selective analyses of chemical species near the sample surface. The detecting point is far from the reaction field and the nascent etch products may diminish by the recombination reaction with other species or at the capillary wall. Additionally, in the case of the inward plasma, the etching gas and etching products go through the most intense part of the plasma in the capillary tube again, and species produced in the capillary tube are observed at the end of it.

One of methods to monitor chemical species near the sample surface is optical emission spectroscopy (OES) which is also commonly used for endpoint detection in plasma etching [6]. However, OES spectrum often contains many spectral lines resulting from both etching gas and etched products and assignments of the species are sometimes difficult. In addition, its information comes from the electronic excited states of the species and not from the ground state. In the present study, we utilized laser induced fluorescence (LIF) to observe a limited domain near the surface in-situ and in real time. With this method, the ground states of the molecules can be observed directly and species-selectively. Thus it may provide additional information on the plasma etching process during the inward plasma etching. We constructed an apparatus with which etching by the inward plasma can be monitored using LIF method. Attempt was mostly concentrated on the detection of SiF_2 during the etching of Si and SiO_2, whose corresponding mass signal at m/z = 66 monitored with QMS did not show intensity change at the SiO_2/Si interface. By observing the LIF spectrum, we have shown that SiF_2 certainly exists near the etched surface of both Si and SiO_2. The plasma gas temperature was derived from the rotational structure of the LIF spectrum. The LIF technique is also used to detect the exposure of the interface of some bi-layer materials (etching endpoint detection of the covering layer).

2. Experiment

Fig. 1 illustrates a schematic diagram of the inward plasma etching and LIF monitoring apparatus. The etching chamber filled with the etching gas was evacuated through a ceramic capillary tube (Alsint 99.7, o.d. $\varphi = 6$ mm, i.d. $\varphi = 4$ mm) with a scroll pump. CF_4 used as the etching gas was fed into the etching chamber through a mass flow controller (Horiba SEC-E40) with the flowing rate of Q. The pressures in the etching chamber (p_1) and in the evacuation chamber (p_2) were monitored with capacitance manometers. An electric field of a radio frequency (13.56 MHz, RF power P_{RF} <50 W) was applied with an electrode surrounding the capillary tube to generate plasma in it. Part of the plasma goes upstream against the etching gas flow and is localized in the gap (Δ < ~1 mm) between the sample and the capillary.

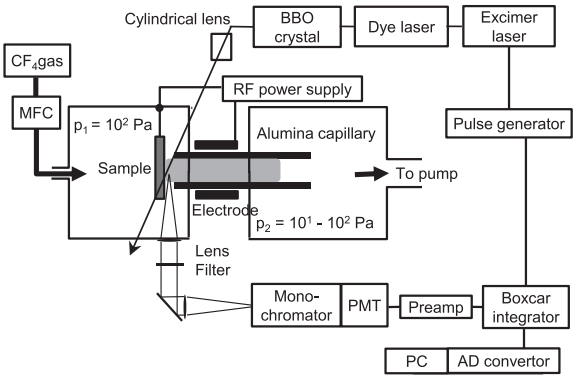

Fig. 1. Schematic diagram of the inward plasma etching and LIF monitoring apparatus.

As for the monitoring system, an output of a dye laser (Lambda Physik SCANMate II) pumped with a XeCl excimer laser (Lambda Physik COMPex100) operated at 10 Hz was frequency doubled with a BBO crystal (~0.05 mJ/~10 ns pulse) and focused by the cylindrical lens (f = 250 mm). Laser beam passed through the narrow gap between the capillary head and the sample surface. SiF_2 was excited through the A-X transition at ~226 nm. Fluorescence emitted was collected from the right angle to the laser beam/the capillary tube with the quartz lens (f = 60 mm) and reflected with a mirror to a monochromator (Nihon Bunko CT-10). The widths of the slits of the monochromator were set to 4 mm and the fluorescence between 240 nm and 260 nm was monitored with a photomultiplier tube (PMT) (Hamamatsu R928). To block the scattered light from the excitation laser, a shortcut filter (Semrock LP02-224R-25) was used. Output of the PMT was fed into the preamplifier and monitored with a digital oscilloscope. The signal was typically averaged over 10 shots with a boxcar integrator and saved in a computer.

3. Results and discussion

3.1. LIF spectrum of SiF_2 in the etching of Si

LIF spectroscopy has been used to detect SiF_2 produced in the reactions of F atom with Si and SiO_2, including the plasma etching using fluorine containing gases [7–10]. In the etching of Si and SiO_2 with the CF_4 inward plasma, SiF_2 existing near the sample surface was also effectively monitored using LIF spectroscopy. Although SiF_2 has three vibrational modes (ν_1: symmetric Si–F stretching, ν_2: F–Si–F bending, and ν_3: antisymmetric Si–F stretching), only ν_2 mode has a large Frank-Condon factor due to the large angle difference between the X and A state and (0,n,0)-(0,0,0) progression with the interval of 250 cm^{-1} is observed [7]. Also, since ν_2 frequency in the X state is small (345 cm^{-1}), $v_2'' = 1$ level has a population of 20% to that of v" = 0 level even at the room temperature and (0,n+1,0)-(0,1,0) hot bands are observed at 95 cm^{-1} lower in energy of the (0,n,0)-(0,0,0) bands [7]. Observed LIF spectra in the present study during the etching of Si and thermally-grown SiO_2, had also such feature and thus were assigned to SiF_2. The observed decay time of the LIF signal was ~20 ns. Taking account of the duration of the laser (~10 ns) and spread time caused by the response of PMT (2 ns), the fluorescence lifetime was less than 10 ns, which is consistent with the reported value of 6.2 ns [9] by Cunge et al. At the pressure in this

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