Cl_2-assisted focused ion beam etching of Al for three dimensional microanalysis

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Chemically assisted ion beam etching (CAIBE) on Al with Cl_2 reactant gas and Ga FIB irradiation was investigated. The sputtering rate and secondary ion intensities are compared for different conditions of the Cl_2 gas pressure. The sputtering rate by a factor of 10 compared with the case of gas unsupplied was achieved. Mechanism of CAIBE is discussed based on the change of secondary ion intensities of Al and Al chlorides.

1. Introduction

The 3D microanalysis with Ga Focused Ion Beam (Ga FIB) uses the technique of mapping cross sections. The shave-off scan of FIB and cross-sectional mapping with the secondary ions or Auger electrons is repeated to obtain the 3D map of the whole volume of the sample [1]. Such 3D microanalysis is restricted to about 10 μm samples for about 30 minutes etching time from the problem of drift of a sample or a beam scanning position. However, the 3D microanalysis domain of, for example, actual IC is the range of several 10 to several 100 μm. When analyzing a 10 times as large sample with the same resolution, 1000 times as long time is required. For this reason, the authors are developing a new technique for high-speed etching system [2], which uses Chemically Assisted Ion Beam Etching (CAIBE) in order to increase sputtering rate [3].

CAIBE is the technique of combination of the physical etching effect by ion beam irradiation and the chemical etching effect by reactant gas. It is known that, in CAIBE, sputtering rate is improved by 10 or more times compared with the usual physical etching [3]. Much work has been reported on CAIBE focused to III-V semiconductor material, such as GaAs [3, 4] and InP [5]. Data have been collected for the combination of various gas and material. Electronic materials, such as GaAs, InP, Si, SiO_2, Cu and W, are the main objects for research. As reactant gas, halogen-related gases, such as I_2, XeF_2, BCl_3, HCl and H_2O have been used. It has been shown by the combination of various reactant gas and material in these researches that surface chemical process has an important role in acceleration of sputtering rate.

However, there are many points still unknown today about mechanism of increasing sputtering rate. In order to apply high-speed etching by CAIBE to more kinds of material from now on, understanding of the high speed etching mechanism is indispensable. Al is an important material for optelectronics and semiconductor. Al has been used for bonding pad of IC. And damage of bonding pad is one of the most important problem for IC process. We have made 3D microanalysis for bonding pad of IC [6], in which 3D mapping required about 24 hours. In this paper CAIBE on Al with Cl_2 reactant gas and Ga FIB irradiation is reported.

2. Experimental

The sample consisted of an Al film with thickness of 2.5 μm evaporated on Si substrates. Evaluation of sputtering rate was performed by measuring the sputtering time before Si^+ was detected by a quadrupole mass spectrometer (SIMS). The experimental pressure in the analysis chamber was 1×10^{-5} to 1×10^{-1} Pa. The Ga FIB was operated under the condition of 25 kV acceleration, 200 pA current, sub-mm beam diameter, 45 degree incidence angle, and 10×14 μm^2 raster scanning. Cl_2 gas was supplied from a nozzle located 2 mm above the sample surface at room temperature. Pressure in the main chamber when Cl_2 gas was unsupplied was less than 1×10^{-6} Pa. Correction factor of 1.1 for Cl_2 relative to N_2 was applied to the pressure measured with the ionization

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vacuum gauge. Effective pressure P_{Cl2} [Pa] of Cl_2 gas on the sample surface was estimated from geometric relationship between the gas nozzle and the sample. In the first, we assume that Cl_2 molecules spread from the point of the nozzle like hemisphere. The number Z_{Cl2} [molecule·s^{-1}·m^{-2}] of Cl_2 molecules that collide with the sample surface of unit area [m^2] per unit time [s] is written as

$$Z_{Cl2}=N_{Cl2}\times\frac{1}{2\pi d^2} \quad (1)$$

where N_{Cl2} [molecule·s^{-1}] is supply of Cl_2 molecules per unit time and d [m] is distance between the nozzle and the sample surface.

Generally the number Z [molecule·m^{-2}·s^{-1}] of colliding molecules on the surface of unit area per unit time is related to the pressure P [Pa], and is given by

$$Z=2.6\times10^{24}\times\frac{P}{\sqrt{M\times T}} \quad (2)$$

where M [Da] and T [K] are molecular weight and temperature,. Finally we obtain

$$P_{Cl2}=Z_{Cl2}\times\frac{\sqrt{M\times T}}{2.6\times10^{24}} \quad (3)$$

Supply of Cl_2 was estimated from the pressure of the vacuum chamber and the exhaust rate. Decrease of effective exhaust was neglected because there were a gate valve and a short L type tube between a turbomolecular pump and an ion gauge.

3. Results and discussion

Figure 1 shows the Cl_2 gas pressure dependence of the sputtering rate. The horizontal axis shows the estimated Cl_2 gas pressure on the sample, and the vertical axis shows the sputtering rate relative to that without Cl_2 supply (sputtering rate of 1×10^{-13} cm^3/s at 200 pA). Sputtering rate increased at the pressure higher than 1×10^{-2} Pa, then sputtering rate saturated at 1×10^{1} Pa. Increase of sputtering rate occurred in two steps. At the first step ($2 \times 10^{-2} – 5 \times 10^{-1}$ Pa), sputtering rate was increased by a factor of 2.5, and at the second step ($1 \times 10^{0} – 1 \times 10^{1}$ Pa), sputtering rate was increased by a factor of more than 3. This result shows, by adjusting the amount of supply of Cl_2 gas, that the CAIBE enhances the sputtering rate by a factor of 10 compared with the case of gas unsupplied.

Figures 2(a) and (b) show the Cl_2 gas pressure dependence of the secondary ion intensity. At 2×10^{-2} Pa, Al^+ intensity was more than 10 times as high as at 3×10^{-3} Pa, while sputtering rate was hardly increased as shown in Fig. 1. This increase of Al^+ intensity in $3 \times 10^{-3} – 2 \times 10^{-2}$ Pa is caused by increase of secondary ionization probability due to chlorine adsorption. In $2 \times 10^{-2} – 2 \times 10^{-1}$ Pa, the increase of Al^+ intensity is almost parallel to that of sputtering rate.

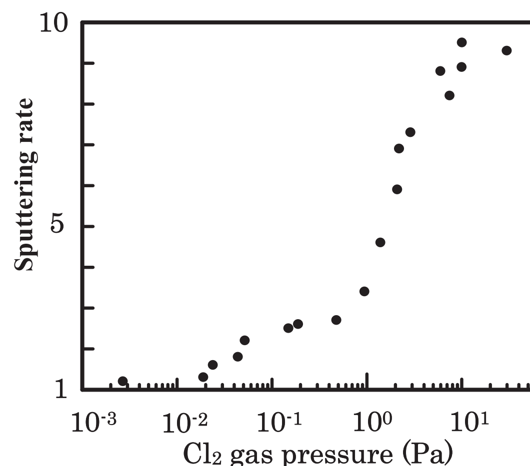

Fig. 1. Chlorine gas pressure dependence of sputtering rate. (beam I=200 pA, beam V=25 kV, scan area=10 × 14 μm^2)

Therefore, increase of Al^+ intensity in $2 \times 10^{-2} –2 \times 10^{-1}$ Pa can be understood as a result of increase of sputtering rate.

Above 1×10^{0} Pa, detected intensities of Al^+ and three kinds of Al-Cl cluster ions were all drastically decreased. In this pressure region actual pressure in the vacuum chamber was above 1×10^{-2} Pa and the mean free path of secondary ions was expected to be shorter than the distance between the sample and the detector. Therefore, this intensity decrease is due to decrease of detection efficiency. The decrease of Al^+ intensity in $2 \times 10^{-1} – 1 \times 10^{0}$ Pa seems to show decrease of Al^+ yield because the mean free path is long enough.

Among three kinds of Al-Cl cluster ions $AlCl_4^-$ intensity behaved differently from that of $AlCl^+$ or $AlCl_2^+$, as shown in Fig. 2(b). Intensities of $AlCl^+$ and $AlCl_2^+$ increased in the pressure range from middle 10^{-3} to 10^{0} Pa, followed by drastic decrease due to decrease of detection efficiency. On the other hand, $AlCl_4^-$ intensity started to increase at middle 10^{-2} Pa and slowly decreased above 10^{0} Pa.

The following mechanism is proposed as a possible explanation of the results shown in these three figures. Different phenomenon on the surface appears to occur in four ranges of $3 \times 10^{-3} – 2 \times 10^{-2}$ Pa, $2 \times 10^{-2} – 2 \times 10^{-1}$ Pa, $2 \times 10^{-1} – 1 \times 10^{0}$ Pa, and above 1×10^{0} Pa. The sputtering mechanism is discussed secondary ion intensity and sputtering rate in each pressure range. In the pressure range between $3 \times 10^{-3} – 2 \times 10^{-2}$ Pa, chemisorbed chlorine increases the surface work function, resulting in increase of positive secondary ionization probability [7]. Atomic ratio of chlorine to surface aluminum is too small to increase sputtering rate. In the range between $2 \times 10^{-2} – 2 \times 10^{-1}$ Pa, chlorine coverage is increased and finally all surface aluminum atoms have one or more chemical bonds with chlorine atoms. Sputtering rate is increased probably because Al-Cl bonds weaken bindings of

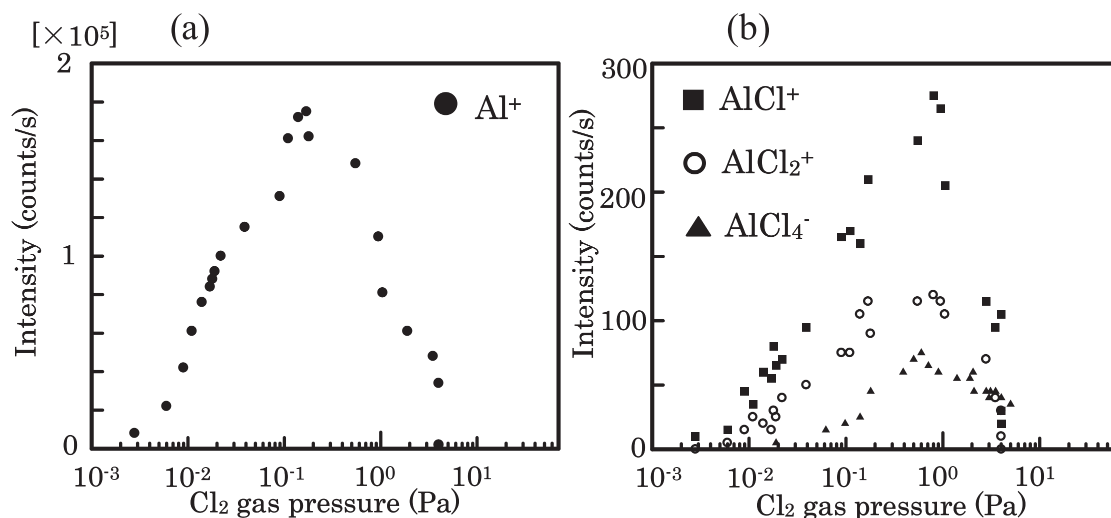

Fig. 2. Chlorine gas pressure vs. various secondary ion intensities.
(beam I=200 pA, beam V=25 kV, scan area=10 × 14 μm^2)

surface aluminum atoms to substrate metallic aluminum. Fully chlorinated aluminum ($AlCl_3$) begins to be formed, resulting in appearance of $AlCl_4^-$ which is a product of Cl^- coordination to $AlCl_3$ as a Lewis acid. In the range between 2×10^{-1} – 1×10^0 Pa, average chlorination number of surface aluminum atoms is increased and finally surface is completely covered with $AlCl_3$. Because atomic ratio of chlorine to aluminum is increased, intensities of Al-Cl cluster ions are increased, while intensity of Al^+ is decreased and pressure dependence of sputtering rate increases from 1st step to 2nd step. In the pressure range above 1×10^0 Pa, $AlCl_3$ film covers the surface. As well known, $AlCl_3$ has relatively high vapor pressure [8] and ion bombardment enhances desorption. It is reported that the amount of chloride coverage with relatively high vapor pressure effects to etching yield [3]. Sputtering rate depends mainly on the formation of $AlCl_3$, and therefore, in low 10^0 Pa range the sputtering rate is proportional to the Cl_2 pressure. Above middle 10^0 Pa desorption rate of $AlCl_3$ and other factors such as scattering of primary Ga^+ ions lead to saturation of the sputtering rate.

4. Conclusions

Detailed discussion on Al CAIBE with Cl_2 gas has been first reported. Increase of sputtering rate by a factor of 10 was observed. By measuring sputtering rate and intensities of various kinds of secondary ions over wide pressure range, data were acquired containing much information on mechanism of CAIBE. From the results the mechanism of CAIBE has been proposed consisting of four pressure regions with distinctive chemical process. This work is expected to contribute greatly to the understanding of the high speed etching mechanism.

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