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Characteristics of Selective Deposition of Metal Organic Films Using Focused Ion Beams

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50 keV Ar^+ or 35 keV focused Ga^+ beam were irradiated in a trimethyl aluminum atmosphere to provide a detailed characterization of maskless deposition. It was found from Anger electron spectroscopy that deposited films contain oxygen, carbon, aluminum and fluorine. The film thickness increased linearly with increasing a dose and the deposition rate was 10-20 nm/(10^{16}ions/cm^2). A 0.5 μm wide fine pattern which reflects a beam profile was formed by using focused Ga^+ beam.

1. Introduction

Focused ion beams provide various possibility of novel applications in addition to maskless ion implantation, maskless etching and scanning ion beam lithography and importance of focused ion beams increases by developing these novel possible applications.

One of the most important approachs to develope these applications is to make use of various ion beam induced chemical effects such as radiation enhanced etching, ion beam modification of materials[1] and ion beam assisted etching[2]. Ion beam assisted etching is a novel etching technique in which etching is done by bombarding ion beams in a reactive gas ambient. Bombardment of ions on a solid surface can enhance adsorption or induce new bonding or bond rapture or sputter off nonvolatile atoms and etching reaction is enhanced. This technique has been applied for maskless etching of GaAs and Si and it was found that the etching rate is enhanced by about 10 times than normal physical sputter etching. It was also found that the etching proceeds by vapourization of volatile reaction products formed with adsorbed reactive gas molecules by ion beam bombardment.

If reaction products are nonvolatile, reactant molecules pile up and film deposition may occur. Such deposition by ion bombardment has been observed for various organic films[3-5].

This can be applied for maskless deposition using focused ion beams, which is attractive for various applications, for example, direct fabrication or repair of lithography masks, electrodes, interconnections or full maskless process for semiconductor device fabrication. It was observed that maskless deposition can be done by bombarding ion beams in trimethyl aluminum (TMA) atmosphere with a relatively high yield of 10-20 atoms/ion[6].

The purpose of the present investigation is to provide a more detailed characterization with respect to parameters of interest to applications of maskless deposition.

2. Experimental procedures

Fig. 1 shows experimental setup for ion beam assisted deposition. 50keV broad Ar^+ or 35 keV focused Ga^+ ion beams were irradiated at room temperature in TMA ($Al(CH_3)_3$) atmosphere through a bore with a diameter of 120 μm formed in 200 μm thick stainless steel plate. The current density was about 1 A/cm^2 for Ar^+ and 100 mA/cm^2 for Ga^+. The vacuum pressure outside the inner sample chamber was 3×10^{-5} torr and 4×10^{-6} torr with and without a TMA flow. For the focused ion beam system, TMA pressure inside the inner sample chamber was directly measured by a thermocoupe guage. The deposition was done on 700nm thick thermally grown oxide or CVD nitride on a Si

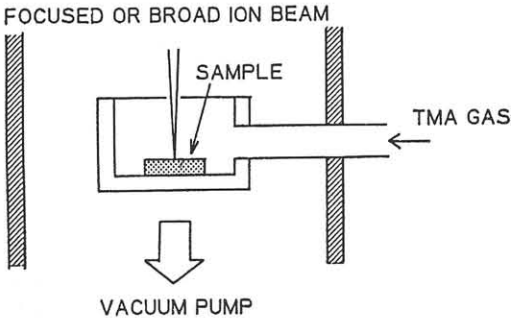

Fig. 1. Experimental setup.

wafer.

Composition and its depth dependence of deposited films were measured by Auger electron spectroscopy (AES) and successive layer removal by 5 keV Ar sputter etching. Samples were exposed to air before measuring Auger electron spectra in order to mount samples in AES chamber. The sputter etching rate are roughly 0.1-0.2nm/min. Film thickness was measured by Dektak and interferometry.

3. Results and discussion

Auger spectra of a deposited film are shown in Fig. 2. The deposition was done on an oxide surface at a dose of $2\times10^{16}/cm^2$ and by 50 keV Ar^+ bombardment. Figs. 2a and b show a spectrum observed at the film surface and a spectrum observed after removing the surface layer for 260 min by Ar sputter etching. The removed thickness corresponds to 26-50nm. From the present measurement, oxygen was also observed in addition to Al and C. It probably came from the residual background gas. The inclusion of oxygen has also been observed in other works[4,5]. The inclusion may be enhanced because reactivity of molecules to reactive residual gas molecules may increase during deposition by ion bombardment. The relative intensity of C to Al was observed to decrease at the surface compared with the inside of the film as can be seen in the figure. The Auger spectrum observed at an unbombarded region is shown in Fig. 2c. Signals both from TMA and Si substrate are observed. Therefore, it can be said that TMA molecules are adsorbed only by a few layers at the sample surface. Fig. 2d shows a spectra observed at an unbombarded region after a sputter etching of 70 min. Adsorbed layers are removed and a signal from Si substrate appears.

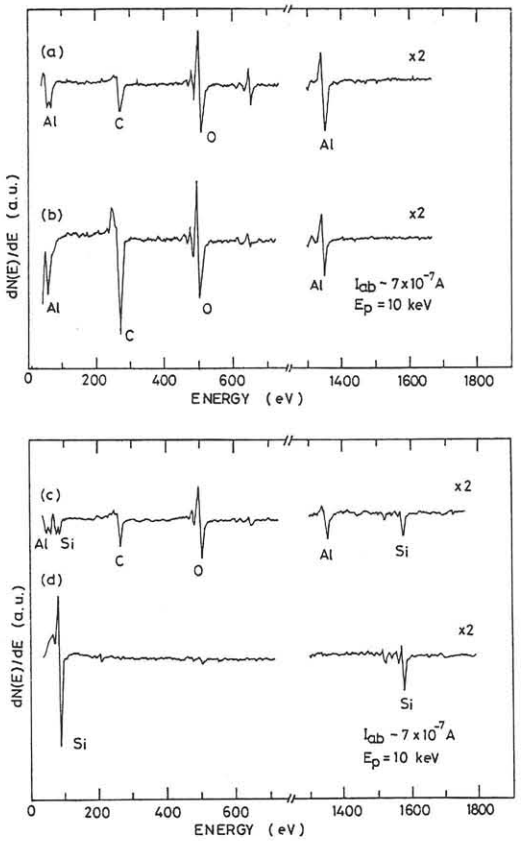

Fig. 2. Auger spectra of bombarded and unbombarded areas by 50keV Ar^+ at a dose of $9\times10^{16}/cm^2$ in TMA atmosphere. (a) bombarded area, (b) bombarded area after sputter etching for 260 min., (c) unbombarded area, and (d) unbombarded area after sputter etching of 70 min.

The peak appeared at an energy of 650eV corresponds to fluorine. This peak was observed at a bombarded region after an etching of 70 min and at an unbombarded region as shown in Figs. 2 b and c. The atomic ratio of F to Al which was estimated from a peak to peak height and a sensitivity ratio of F : Al = 45 : 7 is about 0.1 : 1. At present, it is unknown why fluorine was included in the deposited film, although it is speculated that fluorine was included in TMA gas.

Figure 3 shows an atomic composition ratio of the deposited film as a function of an etching time. The atomic composition ratio was estimated from a peak to peak height of the Auger spectra and using sensitivity ratio of C : O : Al = 8 : 35 : 7. As can be seen in Fig. 3, it was found that the carbon concentration decreased toward the surface, while Al and O distributed almost uniformly over the film thickness measured. The decrease of C at the surface region is not yet understood.

The atomic ratio of Al and C for the deposited

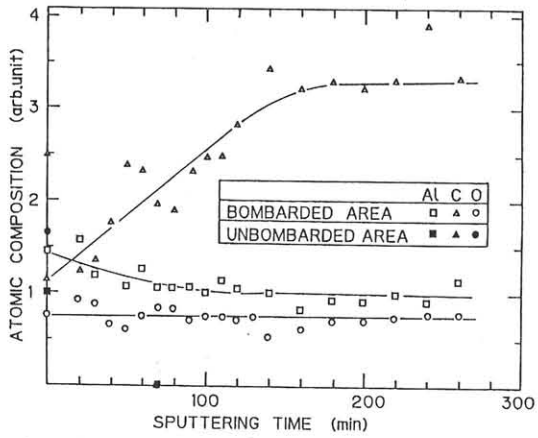

Fig. 3. Depth dependence of atomic composition of deposited films.

film observed after etching for about 150 min agrees with the atomic ratio for TMA. This suggests that the deposition occured by polymerization or carbonization of adsorbed TMA molecules by the ion bombardment. Such polymerization or carbonization have been observed for various organic materials by electron or ion bombardment. The atomic ratio of Al and C for the deposited film observed after etching for about 150 min agrees with the atomic ratio for TMA.

Figure 4 shows a deposited film thickness as a function of a dose. The deposition was done by

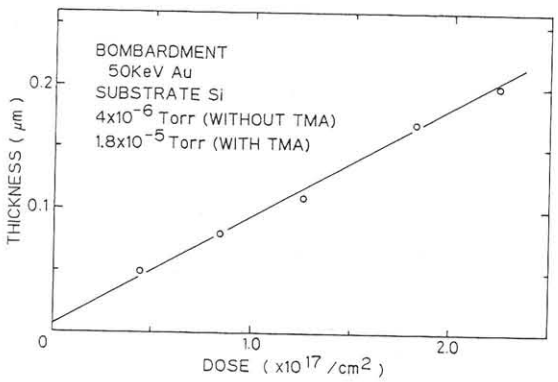

Fig. 4. Deposited film thickness as a function of a dose. The solid line shows a least mean square deviation fit.

50 keV Ar^+ bombardment and at a constant TMA pressure. At a dose range measured, the film thickness increased linealy with increasing a dose. The solid line is obtained by a least mean square deviation fit. The dose vs. film thickness relationship seems to cross at about 7 nm on the vertical axis. This is reasonable if a thin TMA layer condensate on the surface before the ion bombardment. The deposition rate for the present experiment was 10-20 nm/(10^{16} ions/cm^2).

To investigate possiblility for direct pattern deposition and minimum pattern size, 35 keV focused Ga^+ beam was irradiated in TMA atmosphere. Figure 5 shows the delineated line pattern and the cross sectional profile. The

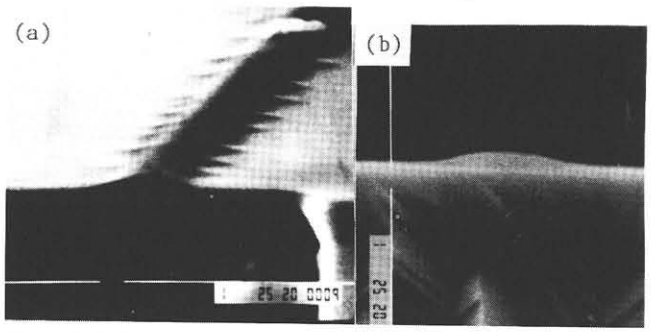

Fig. 5. SEM photograph of a line pattern (a) and a cross sectional profile (b).

pattern was deposited by scanning the focused ion beam at a line dose of$1.3x10^{13}$/cm and at a TMA pressure of 30 m torr inside the inner sample chamber. The deposited pattern profile is like a gaussian and has a linewidth (FWHM) of 0.5 μm. The observed profile reflect a beam profile. This can be said from the observation that the deposited film thickness incerase linearly with a dose as shown in Fig. 4 and also from the result shown in Fig. 6.

Relationship between a beam profile and a deposited pattern profile was measured by depositing a spot pattern to investigate a resolution limit for pattern delineation. Figure 6a shows SEM photographs of deposited and etched spot patterns. The deposition was done on Si_3N_4 layers for various time using 35 keV Ga^+ at TMA pressure of 30 mTorr. The etching was done before an introduction of TMA gas in the inner sample chamber, separated by a few microns from the deposited spot and for the same period with the deposition to estimate the beam profile. Relationship between the deposited and the etched spot sizes and the beam irradiation time is shown in Fig. 6b. If it is assumed that the beam profile has a gaussian profile and the periphery of spots as observed in Fig. 6a corresponds to an equi-dose contour to obtain the contrast in SEM picture, spot radious is given by the equation

$$D_r = it/(\sqrt{2\pi}\sigma e \exp(-r^2/2\sigma^2)$$

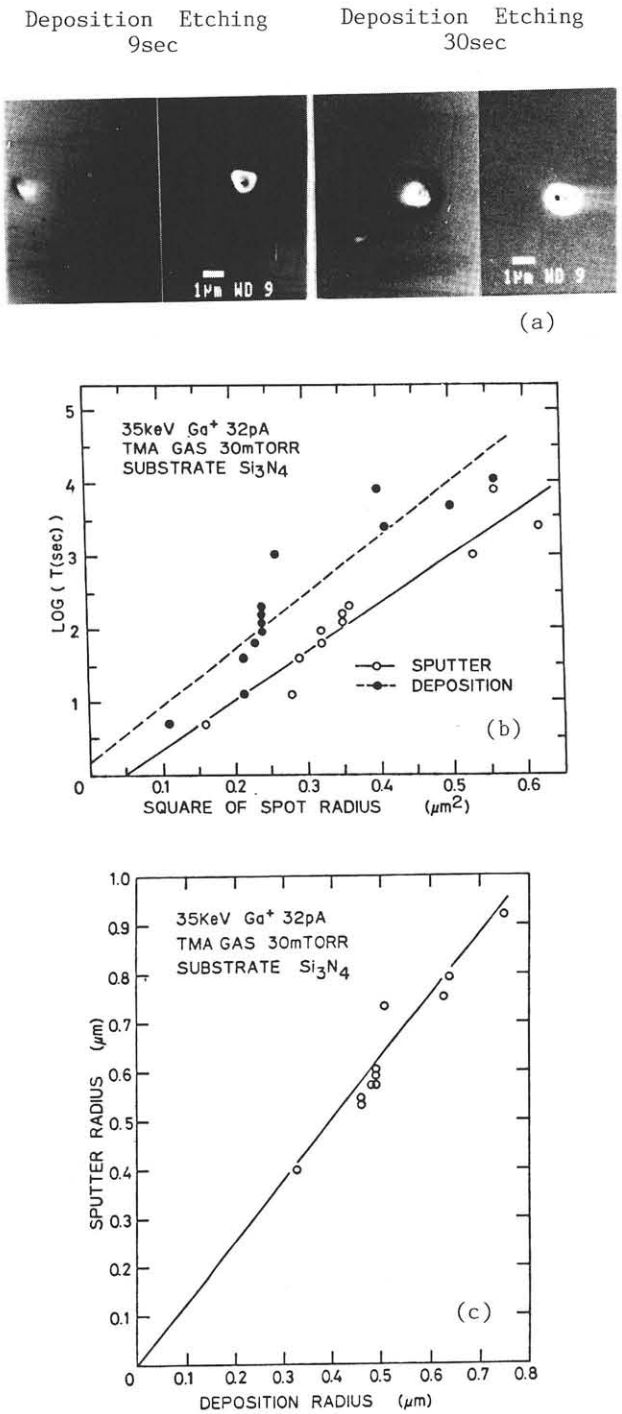

Fig. 6. (a) SEM photographs of deposited and etched spots,(b) deposited and etched spot size as a function of an irradiation time, (c) deposited spot size as a function of etched spot size.

where D_r is a dose required to give the observed contrast in SEM pictures, i is a beam current, t is an irradiation time, e is electronic charge, σ is a beam spreading and r is a spot radius. This equation indicates that the square of the spot size is in proportion to a logarithm of the irradiation time. This is the case as observed in Fig. 6b, though the scatter of the data is large. The solid line in this figure is obtained by a least mean deviation fit. From the fitting, the beam spot size (σ) was estimated to be 0.26-0.28 μm, a value of which was in reasonable agreement from a spot size estimated from the SEM resolution.

The deposited spot size is reploted in Fig. 6C as a function of the etched spot size. This figure also suggests that the deposited pattern profile reflects the beam profile. A more fine pattern may be formed by using fine focused beams.

The present films include much C and O and may not be used for interconnecting low resistivity metal films. However, the present technique is promising in various applications, for example, it can be applied for mask repair or direct mask fabrication for optical, ion or X-ray lithography using focused ion beam. It can be expected from the present result that submicron sized transparent defects are repaired within a few hundredths of a second using a focused ion beam with a current density of $1A/cm^2$. This is 10 times or more faster than a repair by a sputtering.

The inclusion of C and O may be decreased by using other metal compounds and reducing background pressure. A preliminary result using WF_6 gas suggests that W films can be formed by the present technique.

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