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A—2—6 Anodization of Silicon in RF induced Oxygen Plasma

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§1 Introduction

The anodization of silicon in oxygen plasma is very promising since the oxidation at low temperature suppresses the formation of stacking faults[1)] and variation of diffusion profiles. It was first reported by J.F. Ligenza[2)] and was also investigated by other authors[3,4)]. However, neither oxide films as thick as 1μm nor defects in the oxide were studied in detail. Besides, the oxidation mechanism and masking against the oxide growth have remained as important problems for practical application. Here, the conditions for forming thick oxide films in RF oxygen plasma, oxidation mechanism, properties of the oxide, defects in the oxide and Si substrates, and selective oxidation are reported.

§2 Experiments and Discussions

2.1 Oxidation procedures and mechanism : The oxidation was performed with the equipment described elsewhere[5)], at the temperature of 600°C and pressure of 0.2 Torr. oxide films as thicker than 1μm were formed with the constant current of 100 mA/cm^2 within one hour. (Fig. 1)

The oxidation mechanism was studied by measuring the in-depth-profiles of O^{16} and O^{18} ions in the SiO_2 films which were anodized with O^{16} and subsequently done with O^{18}. These profiles indicate that the oxidation has proceeded at both Si/SiO_2 and SiO_2/plasma interfaces through the motion of both silicon and oxygen ions across the oxide. Therefore, the oxidation process here can not be considered as diffusion limited process as discussed by some authors[2,3)]. The high oxidation rate at low temperature is due to the electric field which drifts negative oxygen ions to silicon surface and positive silicon ions to the oxide-plasma interface.

2.2 Oxide properties : The oxide films were of amorphous structure as revealed by electron diffraction patterns, and were found to have the same bonding characters as thermally grown SiO_2 by measuring the Infrared Absoption spectra. The electric breakdown field was as high as about 7×10^6 V/cm.

2.3 Defects in the oxide and substrates

2.3.1 Transmission Electron Microscopy : TEM was used to investigate the Si/SiO_2 interface[6)]. The oxide was clean and no micro-structural defects such as silicon clusters were observed. Besides, the surface roughness was the same as the one of thermally grown Si/SiO_2 interface.

2.3.2 Electron Spin Resonances and C-V method : One ESR line was detected. It had the g-value of 2.000$\sim$2.007 and density of 2$\sim$3 x 10^{12} spins/cm^2.

This defect center was found to be in the region of about 100Å from the Si/SiO_2 interface and was attributed to the surface-states whose density was reduced to less than $10^{11}/cm^2$ by annealing in forming gas at 450°C. (Fig. 2)

2.3.3 Defects in Si substrates : Sirtl etch was done but no oxidation induced stacking fault was observed.

2.4 Selective oxidation : Si_3N_4 film can not be used as oxidation mask since it was oxidized in oxygen plasma[7]. Here, Al_2O_3 was used as oxidation mask.

It was confirmed that Al_2O_3 of 3000Å in thickness was effective in masking against the oxide growth on the silicon surface protected, by measuring the thickness of Al_2O_3 film after the anodization and by observing the bevelled surface with a photo microscope. (photo 1)

§3 Conclusion

The oxidation of silicon in an RF induced oxygen plasma was successfully used to produce oxide as thick as one micron within one hour at temperature of 600°C. It was shown that the oxide was comparable to the best thermally grown oxide. Moreover, in contrast to thermal oxidation, no oxidation induced stacking fault was generated in silicon substrate. Al_2O_3 was found to be useful as mask for selective oxidation. This process is very promising for LSI device fabrication.

References :

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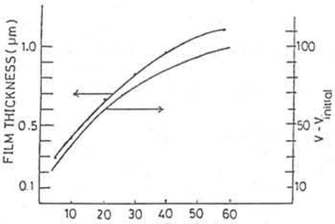

Fig.1 The growth rate of SiO_2 in the anodization with constant current. (T=600°C,I=100mA/cm^2)

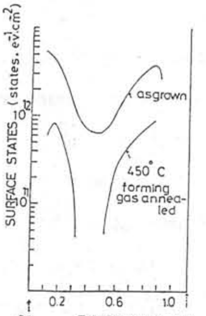

Fig.2 The density of surface states.

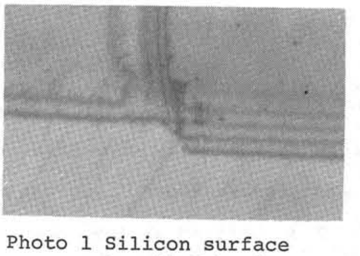

Photo 1 Silicon surface bevelled by 1 degree. (x - 300) Showing Al_2O_3 worked as oxidation mask.