concentration falls simultaneously (4). However, there is no strong evidence for an ion mass effect. The results for Ar/SF_6 and Xe/SF_6 are virtually identical up to 150 eV ion energy. The reduction in the case of He/SF_6 may again be attributed to a lower fluorine concentration.

Conclusion

To conclude, these data support the hypothesis that the etching of Si in an SF_6 plasma is limited by the reaction of fluorine at the surface, whereas the etching of SiO_2 is also dependent on the ion bombardment. Surprisingly, the mass of the ion bombarding the surface has at most a minor effect in both cases. This result is of particular significance for the future development of etching processes in high density low pressure plasmas with independent RF biasing.

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Germanium Atomic Layer Epitaxy Controlled by Surface Chemical Reactions

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Atomic layer epitaxy (ALE) using surface chemical reactions has attracted major interest as a method for the preparation of ultrathin II-VI and III-V compound semiconductor film (1-5). These ALE processes use surface reactions which occur between two kinds of gaseous reactants introduced alternately onto the surface. As a result, each monolayer composed of different elements is produced alternately. This technique is advantageous for closely controlling deposit thickness in terms of the number of process cycles employed. On the other hand, ALE of elemental materials such as Si and Ge has not been developed, although the technique has considerable importance in application to conventional LSI processes. In this paper, a novel layer-by-layer Ge epitaxial growth technique using $GeEt_2H_2$ (Et = C_2H_5) gas surface reaction is proposed and film depositions by this technique are experimentally demonstrated.

Figure 1 explains the proposed technique of the layer-by-layer deposition schematically. A monolayer of $GeEt_2$ formed through $GeEt_2H_2$ gas surface reaction is deposited on the Ge surface at low temperatures (Fig. 1a and b). The top surface is covered with Et groups which protect against further surface reaction (Fig. 1b). After evacuation of the gas, the Et groups are desorbed from the surface by increasing the temperature (Fig. 1c). Thus, a clean Ge monolayer growth is achieved. By repeating this process, a layer-by-layer controlled Ge film can be obtained.

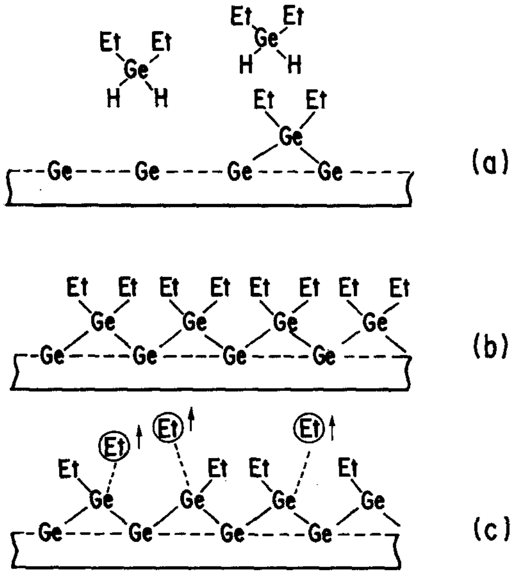

Fig. 1. Reaction model proposed for Ge ALE using $GeEt_2H_2$ (Et = C_2H_5) gas.

A turbomolecular-pumped high vacuum CVD reactor was used for the experiments. Samples set on a quartz boat were heated through a quartz tube by infrared lamp heaters. The base pressure of the reactor was less than 5 × 10^{-8} torr. A quadrupole mass spectrometer (QMS) was used to detect molecules which desorb from the sample surface. A 200Å thick Ge film which was grown epitaxially on the Si (100) wafer through the GeH_4 CVD process was used as the substrate (6). Germanium ALE on the Ge surface was done using pure $GeEt_2H_2$ gas without any carriers.

The $GeEt_2H_2$ gas was introduced on the Ge surface at 220°C in the reactor. The gas pressure and introduction period ranged from 5 × 10^{-4} to 4 × 10^{-2} torr and from 0.1 to 100 min, respectively. Prompt evacuation was carried out to a pressure of 10^{-7} torr. The thermal desorption spectrum (7) of the Et groups was measured by use of the QMS. A typical spectrum (mass = 27) is shown in Fig. 2 for a substrate temperature increase rate of 30°C/min. It was found that the Et groups desorb at temperatures above 400°C. Furthermore, it was observed that both of the desorption temperatures and the Et group desorption yields are al-

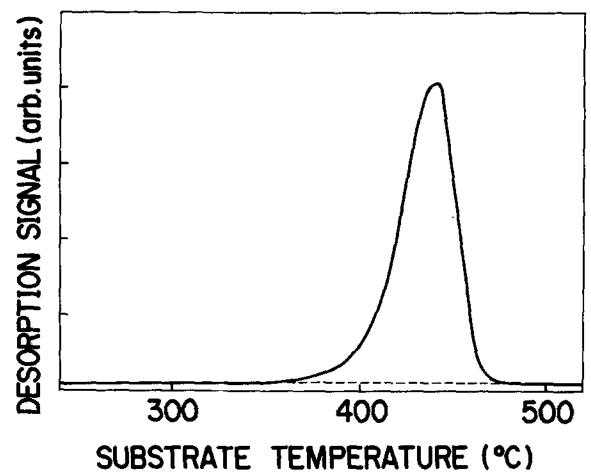

Fig. 2. Thermal desorption spectrum for Et groups on the Ge surface. The rate of substrate temperature increase was 30°C/min.

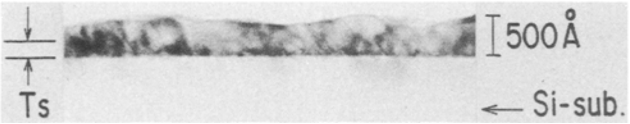

Fig. 3. TEM cross-sectional view of the Ge film grown by the present ALE method. 200 process sequence cycle were grown on the substrate. Thickness of the substrate Ge, T_s, is 200Å.

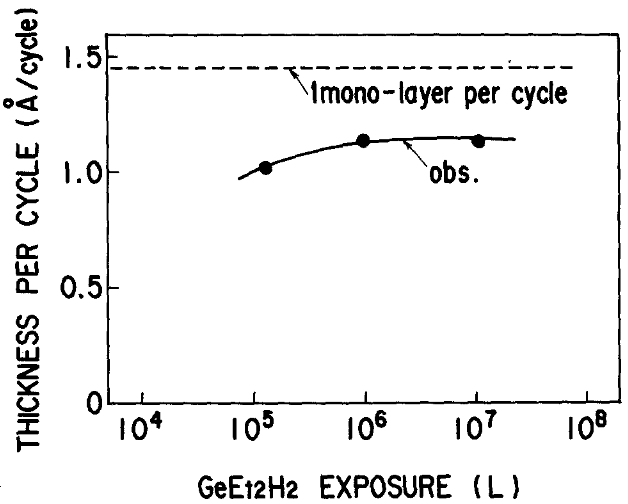

Fig. 4. Observed relation between the Ge film growth thickness per cycle and the $GeEt_2H_2$ gas exposure in the adsorption process. Broken line indicates Ge one monolayer thickness. 1 L = 10^{-6} torr sec.

most independent of the gas pressure and the gas introduction period. The same results were obtained for the samples prepared at the gas introduction temperature range of 100°-300°C. These facts suggest that a $GeEt_2$ monolayer is formed on the Ge surface through the $GeEt_2H_2$ gas surface reaction in a temperature range of 100°-300°C, and the Et groups on the top surface can be desorbed at temperatures above 400°C. Furthermore, no increase of Ge film thickness is observed even for the 100 min gas exposure in 4×10^{-2} torr at 220°C. This indicates that the surface Et groups are stable enough to protect against the further reaction of $GeEt_2H_2$ gas on the $GeEt_2$ monolayer.

A layer-by-layer controlled Ge deposition was carried out using the following process sequence. One cycle of the sequence consists of four processes; namely, gas introduction, gas evacuation, substrate heating and cooling. The $GeEt_2H_2$ gas was introduced on the Ge surface at 220°C at a pressure of 1×10^{-3}-1×10^{-1} torr. Then, after prompt evacuation to 10^{-7} torr, the substrate temperature was increased to 510°C. Each processing period (t_0) was 90s, an interval long enough to evacuate the gases and desorb the Et groups. The residual $GeEt_2H_2$ gas pressure below 10^{-7} torr is negligible for Ge growth, since it was confirmed that the Ge deposition rate was less than 10^{-2} A/min in a $GeEt_2H_2$ pressure of 10^{-7} torr at 500°C. Figure 3 shows a TEM cross-sectional view of Ge film grown in 200 of the process cycles described above. The average Ge growth thickness per cycle was measured from TEM cross-sectional views as a function of the $GeEt_2H_2$ gas exposure and the results are shown in Fig. 4. It is known that the growth thickness per cycle does not depend on gas exposure above 10^6L, and is about 1.2A, which is nearly one Ge monolayer per cycle. Epitaxial growth of Ge on the Ge (100) substrate was confirmed from the electron diffraction patterns. It is thus apparent that Ge ALE can be achieved.

The surface morphology of the grown Ge film, as shown in Fig. 3, is poor. It is considered that the rugged surface is probably due to condensation of deposited Ge atoms during the Et group desorption process at 500°C and/or the influence of oxidation by residual oxygen gas from the base pressure of 5×10^{-8} torr.

In conclusion, possibility of layer-by-layer controlled Ge epitaxial growth is demonstrated in principle using surface chemical reactions of nonsymmetrical structural $GeEt_2H_2$ gas. This technique is based on the repetition of a sequential process consisting of gas introduction on the Ge surface at 220°C, gas evacuation, and Et group desorption at temperatures over 400°C.

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