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Low-Temperature Silicon Epitaxy without Substrate Heating and Selectivity Inversion in Ultraclean ECR Plasma Enhanced CVD

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Si epitaxial films were grown on Si without substrate heating by ultraclean ECR Ar plasma enhanced decomposition of SiH_4. The transition from deposition to etching on Si and SiO_2 was found to occur with the different H_2 addition to the Ar plasma. Thus, selective deposition/etching can be achieved by selecting the amount of H_2 gas addition even in plasma processing. Furthermore, when the plasma conditions were changed, the selective deposition modes were inverted from selective Si epitaxy on Si to selective Si film deposition on SiO_2 only. The surface reaction is discussed based on the XPS analysis.

1. INTRODUCTION

Si epitaxy as well as selective deposition at low temperatures are extremely important for the fabrication of future semiconductor devices. However, so far, substrate heating has been necessary to achieve Si epitaxy. Plasma processing is frequently used in order to lower the process temperature. However, it tends to break selectivity in most cases. Selective plasma deposition has been reported in limited cases such as diamond homoepitaxy at high temperatures (~900°C),[1] and GaAs heteroepitaxy on Si at 630°C by ECR-MBE method.[2] There has been no report up to now on selective plasma deposition of Si at low temperatures.

In our recent study,[3] using ultraclean ECR plasma processing, low-temperature Si epitaxy without external substrate heating was realized for the first time by Ar plasma enhanced decomposition of SiH_4 under a low-ion-energy, i.e. damage-suppressing condition. Moreover, it is found that exposure of the wafer to the H_2 added Ar plasma just before deposition is extremely effective to obtain the clean Si surface. In the present study, the effects of H_2 addition to the Ar plasma during decomposition process of SiH_4 have been investigated, and selective plasma enhanced deposition without substrate heating has been achieved for the first time. Also, selectivity inversion from Si epitaxy on Si only to Si film deposition on SiO_2 only has been performed by changing only the plasma conditions.

2. EXPERIMENTAL

The ultraclean ECR plasma apparatus used has been described previously.[4] The ultimate vacuum of the chamber generated by an oil-free turbo molecular pumping system is $5x10^{-9}$ Torr. The wafer susceptor was not externally heated at all throughout this study. All gases used are of ultraclean grade.[5] SiH_4 gas was introduced into the deposition chamber, which is separated from the plasma generating chamber by a plate with a 100mmϕ window. Ar and H_2 gases were introduced into the plasma generating chamber, and the generated ions are carried to the wafer by a divergent magnetic field without using an ion extraction electrode. In the present study, the 2.45GHz-microwave power was 150 and 700W and the total pressure was 2 and 6mTorr.

The substrates used were Si (100) with patterned thermal SiO_2 films. After cleaning in several cycles in a 4:1 solution of H_2SO_4 and H_2O_2, and DI water, the samples were treated in ~2% HF to remove the native oxide and rinsed with DI water just before loading into the ECR chamber. Plasma pre-exposure for cleaning was not at all executed in the present study. Deposited and etched thickness was measured by Tencor Alpha Step, with a partial removal of the deposited films and/or masking SiO_2 by wet chemical etching if necessary. The etched thickness of SiO_2 was also determined from the difference in ellipsometric measurements before and after processing. The structure of the film surface was evaluated by reflection electron diffraction in the [011] direction of the electron incidence. Scanning electron microscope (SEM) observation and X-ray photoelectron spectroscopy (XPS) analysis have also been performed.

3. RESULTS AND DISCUSSION

When SiH_4 is decomposed by ultraclean ECR Ar plasma without H_2 addition, nonselective Si film deposition was observed both on Si and SiO_2.[3] Figure 1 shows the electron diffraction patterns of the films deposited on Si and SiO_2 under a typical condition without substrate heating. The pattern of the film on Si shows Laue reflection spots indicating single crystallinity, whereas the pattern on SiO_2 shows halo which indicates an amorphous film.

With the addition of H_2 to the Ar plasma, the deposition rate decreased and finally deposition was inverted into etching. Figure 2 shows the added H_2 flow rate dependence of the deposition/etch rates for four different conditions. The transition from deposition to etching on Si and SiO_2 is found to occur at different H_2 additions. Thus, selective deposition/etching has been achieved by selecting the H_2 gas addition, as indicated by arrows even in plasma enhanced processing.

Figure 2 also contains the electron diffraction pattern of the deposited films under typical selective deposition conditions indicated. Figure 3 shows cross sections of the typical selectively deposited films on (a) Si and (b) SiO_2. It is clearly seen in these figures that when the plasma conditions (total pressure and microwave power) are changed, the selective deposition modes can be in-verted: Si selective epitaxy on Si only (Fig. 2a,3a) occurs under the condition of 2mTorr and 700W, where SiO_2 is slightly etched, while selective deposition of polycrystalline(Fig. 2b,3b) and amorphous(Fig. 2c,d) Si films on SiO_2 only occurs for 6mTorr or 150W, where the Si substrate is etched.

It is known that the typical peak energy of ions in the ECR system is a few eV at about 2mTorr and lower at higher pressures, and the plasma density is higher at higher microwave power.[6] Thus, the condition for Si selective epitaxy includes a higher ion energy and a higher plasma density than that for polycrystalline/amorphous Si deposition. On the other hand, the authors already showed that the plasma exposure at a lower pressure (0.2mTorr), where the ion energy is high, causes damage on the Si surface and suppresses the epitaxial growth.[3] Therefore, the optimum plasma condition for plasma-enhanced epitaxy is present.

Figure 4 shows XPS spectra of Si atoms on the masking SiO_2 surface measured for the sample with selective epitaxy on Si. Just after exposure to the plasma, the Si^0 peak is observed in addition to the Si^{4+} one. By subsequent exposure to air, the Si^0 peak height decreases, although the Si^{4+} peak scarcely changes. When SiH_4 was not introduced, this Si^0 peak on SiO_2 was missing and a higher SiO_2 etch rate was observed. Thus, the active Si^0 atoms on the SiO_2 surface originate from SiH_4 and they suppress etching of the masking SiO_2 in Si selective epitaxy.

When the plasma was generated under a condition where amorphous Si is deposited selectively on SiO_2, but where the shutter was closed, interrupting the direct incidence of ions, about 80% of the usual Si etch rate was observed with no Si deposition on SiO_2. Therefore, it is considered that in selective deposition of amorphous Si on SiO_2 Si is etched mainly by radicals, and deposition of amorphous Si on SiO_2 is induced by incident ions. Ion incidence seems to play a different role in the reactions on Si substrates and on amorphous Si on SiO_2.

4. CONCLUSIONS

Even without substrate heating, Si epitaxial films were grown on Si by ultraclean ECR Ar plasma enhanced decomposition of SiH_4, while films deposited on SiO_2 were amorphous. The transition from deposition to etching on Si and SiO_2 was found to occur at different amounts of H_2 addition to the Ar plasma. Thus, selective deposition/etching was achieved even in plasma processing by adjusting the H_2 gas addition. Furthermore, when the plasma conditions were changed, the selective deposition modes were inverted from Si selective epitaxy on Si only to selective Si film deposition on SiO_2 only. In selective Si epitaxy, the Si^0 atoms, originating from SiH_4, were observed on the masking SiO_2 surface by XPS analysis. These Si^0 atoms cause suppression of SiO_2 etching. In selective deposition of amorphous Si on SiO_2, Si substrate was etched mainly by radicals.

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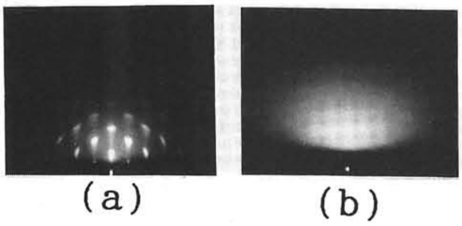

Fig. 1. Electron diffraction pattern for (~600 A) Si films deposited on Si (a) and SiO_2 (b) without substrate heating by ultraclean ECR Ar plasma enhanced decomposition of SiH_4.

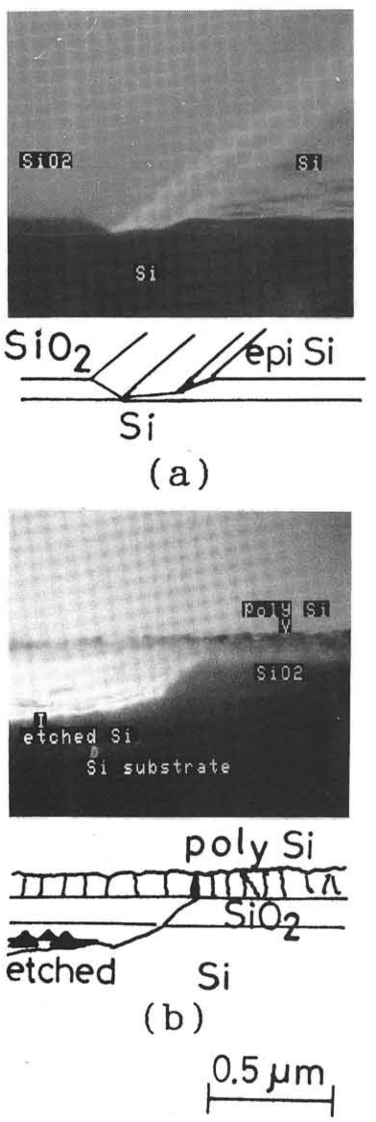

Fig. 3. SEM photographs of selectively deposited films. (a) Selective epitaxy on Si with SiO_2 etching (2mTorr, 700W). (b) Selective deposition of polycrystalline Si on SiO_2 with Si substrate etching (6mTorr, 700W).

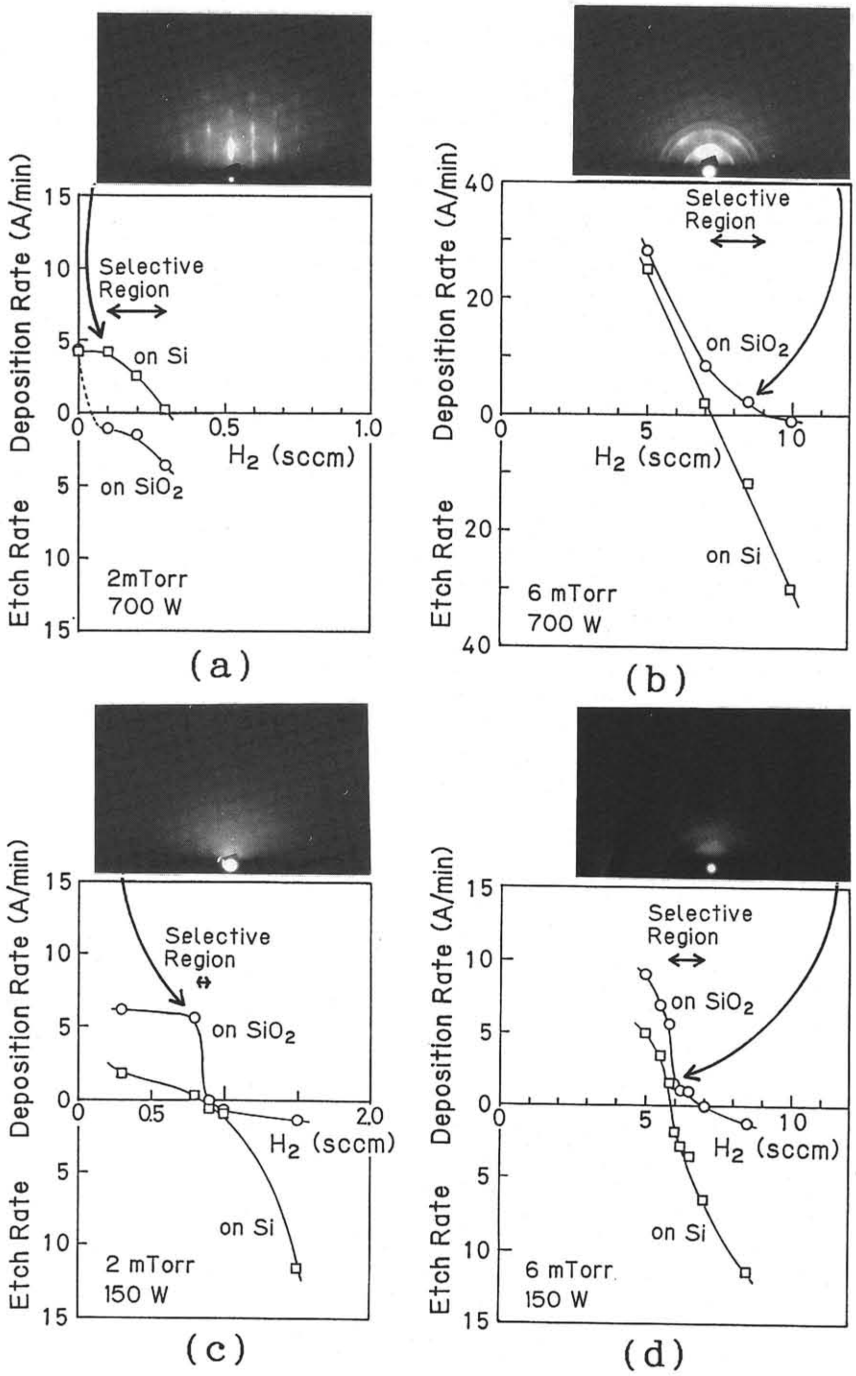

Fig. 2. Dependence of deposition and etch rates on added H_2 flow rate for four different plasma conditions. Electron diffraction pattern for the indicated samples are also shown.

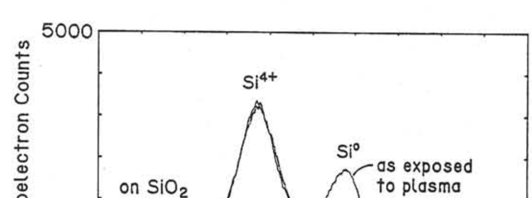

Fig. 4. XPS spectra of Si atoms at the SiO_2 surface exposed to the plasma under a selective epitaxial condition for the same sample as that in Fig. 3(a).