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The Orientation Dependence of Impurity Sticking on Si Molecular Beam Epitaxy

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A study has been made on dependence of Ga and Sb sticking coefficients on substrate orientation in Si molecular beam epitaxy. The concentrations of Ga and Sb in the (111) epitaxial films are found to be higher than those in the (100) ones, the phenomena of which are caused by the dependence of the sticking coefficients and the formation of the ad-layer on substrate orientaton relative to Ga doping and to Sb doping, respectively.

From the study, it has been confirmed that the (111)epitaxial film can incorporate various impurities more frequently than the (100) film, and that the incorporated impurities can increase crystal defects densities.

1. Introduction

In an epitaxial Si film growth using molecular beam epitaxial (MBE) technology, it has been confirmed that the crystal defect density depends generally on the substrate orientation. In the previous presentation, we explaired the relationship between the two factors and came up with the result that the defect density with the (100) oriented substrate was much smaller than that with the (111) oriented substrate. In the same presentation, we referred to the fact that the carrier concentration of the unintentionally-doped, (111) oriented epitaxial film was ten times higher than that of the unintentionally-doped, (100) oriented epitaxial one (1). These phenomena suggest that residual gases like CO and CO_2 in the ultra-high vacuum chamber are responsible for the contamination, of which absorbed amount in the epitaxial film is dependent on the substrate orientation. In fact, however no study has yet verified the direct relationship between crystal defect and the amount of carbon contamination (2),because the detection limit of carbon didn't meet the requirement.

In order to confirm the orientation dependence of carbon adhesion, we examined the substrate orientation dependence of Sb and Ga adhesion to the silicon surface.

2. Experiment

These experiments were repeated using CZ-76mmφSi, either (111) or (100), N and P type substrates for Ga and Sb doping, respectively. After being boiled in NH_4OH/H_2O_2 and rinsed in deionized water, substrates were subjected to spin-dry and then charged into the ultra-high vacuum chamber. The natural oxide was removed for 2 minutes in Rad clean process (3) at 800°C. Then the substrate temperature was set to the epitaxial temperature and 1 micron thick epitaxial film was grown at about 0.6nm/sec. During the growth Ga and Sb were supplied by using Knudsen-cells.

Depth profiles of chemical concentration relative to both Ga and Sb and carrier concentration were measured by a SIMS and 4 point probing method, respectively. The epitaxial surfaces were analyzed with an AES which was equipped in the preparation chamber, just after its growth.

3. Results and Discussion

Figure 1 shows the carrier concentration distribution of the Ga-doped epitaxial films on the (111) and (100) oriented substrates. The Ga doping was carried out at the substrate temperature of 700°C and Knudsen-cell temperature of 700°C. The average carrier concentrations of the (111) and (100) oriented

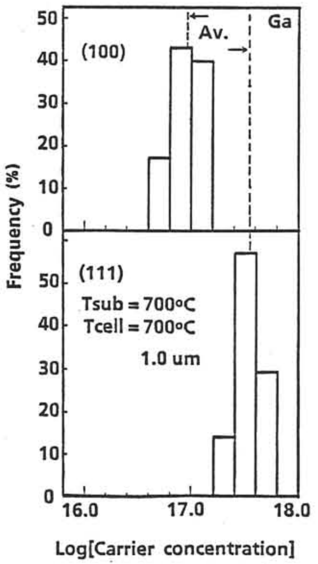

Fig.1 Carrier concentration distribution of Ga doped epitaxial film grown on the (111) and (100) oriented substrates at the substrate temperature of 700°C.

epitaxial films were $3.5x10^{17}/cm^3$ and $9.2x10^{16}/cm^3$, respectively. The carrier concentration of the (111) epitaxial film is about 4 times that of the (100) epitaxial film. This orientation dependence of the carrier concentration is related to the dependence of the sticking coefficient of Ga. The contribution of the unintentionally-doping, however, should be counted on, because the carrier concentrations, even without using the Ga Knudsen-cell, were approximately $1x10^{16}/cm^3$ for the P type and less than $1x10^{16}/cm^3$ for the N type with the(111) and (100) epitaxial films, respectively(1).

In order to confirm the dependence of the sticking coefficients of Ga on the substrate orientation, we investigated the chemical concentration of Ga by a SIMS. Figure 2 shows depth

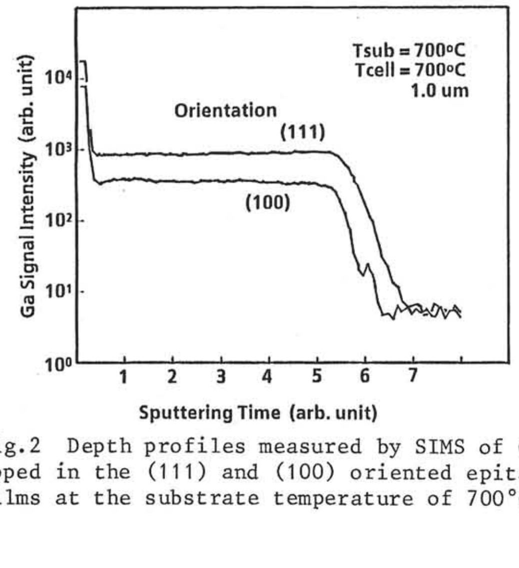

Fig.2 Depth profiles measured by SIMS of Ga doped in the (111) and (100) oriented epitaxial films at the substrate temperature of 700°C.

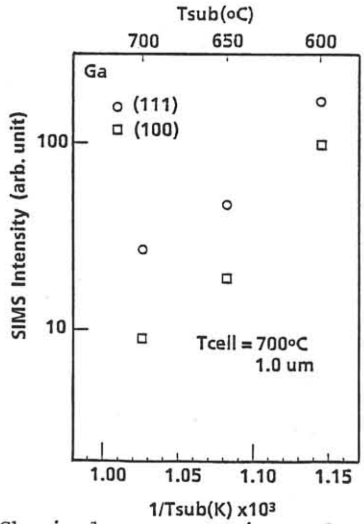

Fig.3 Chemical concentrations of Ga at the 0.5μm deep from the epitaxial surface measured by SIMS in the (111) and (100) oriented epitaxial films at the substrate temperature of 600°C, 650°C and 700°C.

profiles of relative Ga chemical concentration in the (111) and (100) oriented epitaxial films at the substrate temperature of 700° C. The depth profiles of Ga chemical concentration at the substrate temperature of 600° C and 650°C represent almost flat, similar to that at 700° C. Figure 3 shows relative Ga chemical concentration at the depth of 0.5 micron from the epitaxial surface with the (111) and (100) oriented substrate, which actually represents total concentration of Ga chemical in the epitaxial film. It is clear that the Ga chemical concentrations in the (111)epitaxial films are larger than those in the (100) ones at the substrate temperature at 600° C through 700° C.

These results clearly indicate that sticking coefficient of Ga to the (111) silicon surface is larger than that to the (100) surface as long as the substrate temperature remains at 600° C through 700° C. Table 1 shows the carrier concentrations of the(111) and (100) epitaxial films and some related factors for both films. At the

Table 1. Carrier concentration ratio and chemical concentration ratio of Ga doped in the (111) and (100) epitaxial films, respectively.

Tepi(°C)	Carrier Concentration (cm^{-3}) (111)	(100)	Ratio	Chemical Concentration ratio
600	8.0×10^{17}	8.4×10^{17}	0.95	1.7
650	9.4×10^{17}	1.8×10^{17}	5.22	2.5
700	5.3×10^{17}	9.0×10^{16}	5.88	3.0

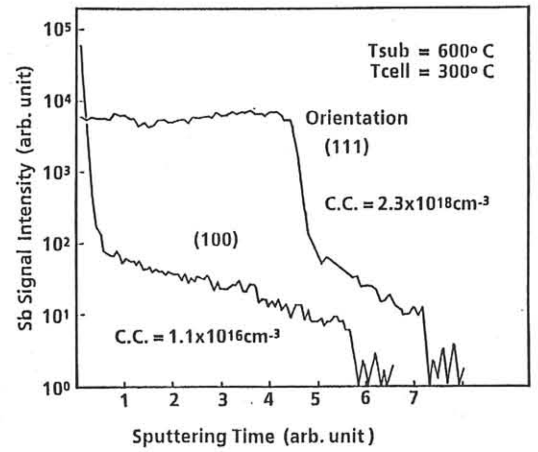

Fig.4 Depth profiles of Sb doped in the (111) and (100) oriented epitaxial films grown at the substrate temperature of 600°C.

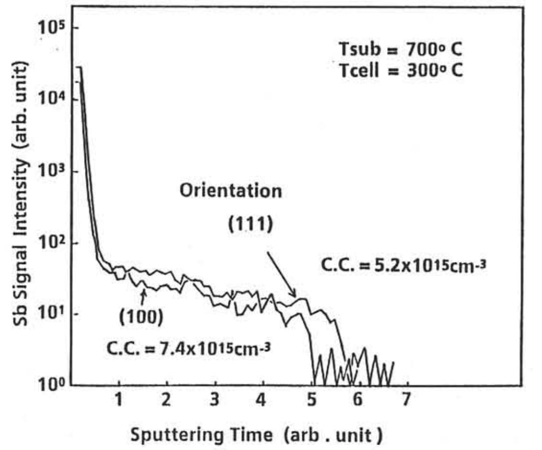

Fig.6 Depth profiles of Sb doped in the (111) and (100) oriented epitaxial films grown at the substrate temperature of 700°C.

substrate temperatures of 650° C and 700° C, the chemical concentration ratios are smaller than carrier concentration ratios. This is thought to be caused by the contamination from the Ga Knudsen-cell. In addition, due to the drastic decrease of the efficiency of Ga doping at the substrate temperature of 600° C (4), the carrier concentration of the (111) film is about the same as that of the (100) one.

Orientation dependence of Sb doping has also been studied. The doping was carried out at the substrate temperatures of 600° C, 650° C and 700° C and at the Knudsen-cell temperature of 300° C. Figures 4,5 and 6 show depth profiles of Sb with the carrier concentrations in the (111) and (100) epitaxial films grown at the substrate temperatures of 600° C, 650° C and 700° C. The chemical concentrations of Sb in the (111) epitaxial films are higher than those in the (100) ones at the substrate temperatures of 600° C and 650° C, but there is no difference in the concentrations when the substrate temperature comes to 700° C. It is naturally understood that the orientation dependence is very similar to that of the carrier concentration.

To find the cause of such significant difference in the chemical and carrier concentrations of Sb between (100) and (111) oriented epitaxial films, as compared with the case of Ga, the ad-layer (5) of Sb was examined by a AES. Figure 7 shows the Auger spectra of Sb-doped epitaxial films grown on (111) oriented substrate at the substrate temperature of 650° C and at the Knudsen-cell temperature of 300° C. Peaks of Sb (MNN) and Si (LVV) were observed at the Auger electron energy of 455eV and 92eV, respectively. Based on these data and the assumption that the thicknesses of the ad-layer are 3.1Å for (111) and 2.7Å for (100) which are thickness of one monolayer, Sb concentratin in the ad-layer was calculated as shown in Table 2. Table 2

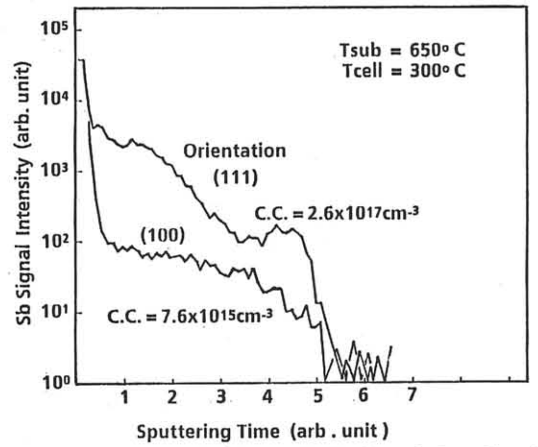

Fig.5 Depth profiles of Sb doped in the (111) and (100) oriented epitaxial films grown at the substrate temperature of 650°C.

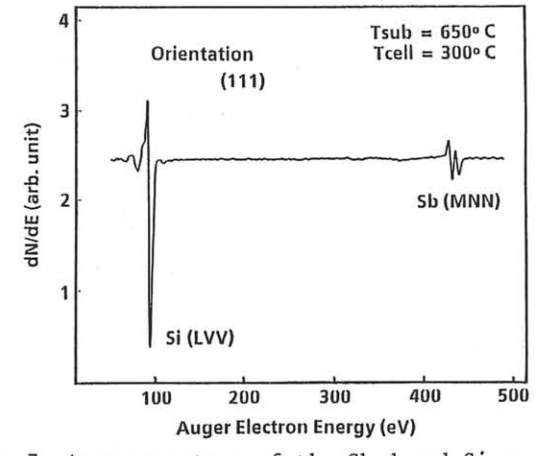

Fig.7 Auger spectrum of the Sb doped Si surface just after the epitaxial growth.

Table 2. The values of Sb concentration in the ad-layer, Sb sheet concentration in the epitaxial film and sheet concentration ratio.

Tsub (°C)	Orien-tation	Sb concen-tration in the ad-layer (cm^{-2})	Sb sheet con-centration in the epi film (cm^{-2})	Sheet con-centration ratio (111)/(100)
600	(111)	1.4×10^{13}	1.0×10^{14}	160
	(100)	1.7×10^{14}	6.4×10^{11}	
650	(111)	1.3×10^{14}	2.3×10^{13}	38
	(100)	1.5×10^{14}	6.0×10^{11}	
700	(111)	1.3×10^{14}	2.8×10^{11}	1
	(100)	1.1×10^{14}	2.8×10^{11}	

also includes the incorporated Sb sheet concentration into the epitaxial film of the integral of the SIMS profile and the sheet concentration ratio of the (111) epitaxial film to the (100) one.

These results clearly indicate that large portion of Sb atoms on the (100) surface made the ad-layer and only small portion of Sb atoms was incorporated into the epitaxial films. This phenomenon also became significant on the (111) surface at 700° C. The incorporated portion, however, increased as the substrate temperature decreased, and at 600° C large portion of Sb was incorporated into the epitaxial film.

To confirm the sticking coefficient of Sb, we estimated the total concentration of sticking Sb, which is consisted of the amount of Sb existing in the ad-layer and the sheet concentration of the epitaxial film, based on the Allen's model (5). It was found that the total concentrations of Sb between in the (111) and in the (100) epitaxial films were comparable at the substrate temperature of 600° C through 700° C, which led us to think that the differencebetween the sticking coefficients of Sb to the (111) surface and to the(100) one is no longer a significant factor. Actually, the difference is thought to be within several times at the most. Therefore the formation of the ad-layer becomes a contributing factor to a large value of the Sb chemical concentration ratio as compared with Ga, which also give rise to the difference of carrier concentration between the (111) and the(100) epitaxial films.

4. Conclusion

The orientaion dependence of Ga and Sb sticking coefficients to the epitaxial surface has been revealed by a SIMS, an AES and the carrier concentration measurements. Both the carrier and the chemical concentrations of Ga in the (111) epitaxial film were higher than those in the (100) one at the substrate temperature 600° C through 700° C. This fact is related to the sticking coefficients on the substrate orientation. In the case of Sb doping that was treated at below the substrate temperature of 700° C, the amount of Sb in the (100) ad-layer was larger than those in the (111) one, and only small portion of Sb was incorporated in the (100) epitaxial films as compared with the (111) ones. At 700° C the amounts of Sb in both the surface ad-layers and the epitaxial films were not dependent on the substrate orientaion. This is because the distribution factor of Sb between in the ad-layer and in the epitaxial film has the orientaion dependence.

These results suggest that contaminations incorporated in the (100) epitaxial film were less than those in the (111) one, and that this fact decreases the defect densities in the (100) epitaxial film. This can support one of our predictions that the sticking of other impurities including carbon has the similar orientaion dependence, and that these impurities behave as nuclei of crystal defects and as source of unintentionally doped acceptors in epitaxial films, grown especially on (111) oriented substrate.

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