Growth Mechanism of SOI-GaAs Films on CaF₂/Si Structures in the Electron-Beam Exposure and Epitaxy (EBE-Epitaxy) Technique

Hee Chul LEE, Tanemasa ASANO, Hiroshi ISHIWARA and Seijiro FURUKAWA

Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuda, Midoriku, Yokohama 227

We investigate the surface modification effect of CaF_2 surfaces by electron beam (e-beam) exposure in order to clarify the growth mechanism of the EBE-epitaxy (Electron-Beam Exposure and Epitaxy) for $GaAs/CaF_2/Si(111)$ structures. It is found that As atoms of the order of monolayer are adsorbed on the surface of CaF_2 film exposed to an e-beam, but not adsorbed to the unexposed surface even though both of these CaF_2 surfaces were impinged by an As_4 flux under the same condition. It is also found that the amount of As atoms adsorbed on the CaF_2 surface has a strong correlation with the quality of top GaAs films. Thermal stability and distribution of the As atoms on the CaF_2 surface are also examined.

§1. Introduction

A GaAs SOI(semiconductor-on-insulator) structure on Si substrate is attractive for high speed ICs (integrated circuit), opto-electronic ICs and 3-dimensional ICs. For the formation of the SOI structure, a variety of methods have been studied actively. Among them, heteroepitaxy method by which GaAs films can be grown at a relatively low temperature, is one of the best methods to fabricate the GaAs-SOI structure since it can provide stoichiometric good films.

From this viewpoint, we have investigated the GaAs/insulator/Si structure using fluoride. 1-2) However, it was difficult to obtain a thin GaAs film having good quality because the growth of GaAs on CaF₂ was initiated by the three-dimensional growth and the crystalline quality of the film degraded near the interface between GaAs and CaF₂. Recently, we developed a novel heteroepitaxy method, EBE-epitaxy (Electron-Beam Exposure and Epitaxy), which is very useful for growing SOI-GaAs films with excellent crystallinity on CaF₂/Si (111) structure. 3-5) In this method, the surface of CaF₂ films is first modified by

electron-beam (e-beam) exposure under arsenic (As) impingement, then excellent GaAs films are grown on the modified CaF, surfaces.

In this presentation, in order to clarify the growth mechanism of the EBE-epitaxy, we study how the surface of CaF₂ film is changed by exposure of an e-beam under As impingement, and also investigate the relation between the CaF₂ surface modification and the quality of top GaAs films.

§2. Experimental Procedure

Detailed growth process of the EBE-epitaxy for GaAs/CaF₂/Si(111) structures was described in ref. 3. In brief, single-crystal CaF₂ films were grown on (111) oriented Si substrates at 700°C. Then, the surfaces of the CaF₂ films were exposed to a 3keV e-beam under impingement of As₄ flux. Finally, 320nm thick GaAs films were grown on the CaF₂/Si structures at 550°C.

In order to investigate the surface modification of ${\rm CaF_2}$ film in the EBE-epitaxy, we prepared ${\rm CaF_2}/{\rm Si}(111)$ structures in which the surface of ${\rm CaF_2}$ was exposed to an e-beam at various doses under As impingement. The typi-

cal current density of an e-beam was about 1- $10\mu\text{A/cm}^2$. The temperature of CaF_2/Si structures was brought to 550°C during the e-beam exposure, and then the sample was kept in the As₄ flux down to 300°C. Rutherford backscattering spectroscopy (RBS) measurements were performed using 1.5MeV $^4\text{He}^+$ ions to examine the change of the modified CaF_2 surface. The glancing angle method in RBS was also used for acheiving higher depth resolution.

§3. Results and Discussion

Figure 1 shows RBS random and aligned spectra of CaF₂ films grown on the Si(111) substrates. In this figure, both samples were impinged by an As₄ flux at 550°C, but only

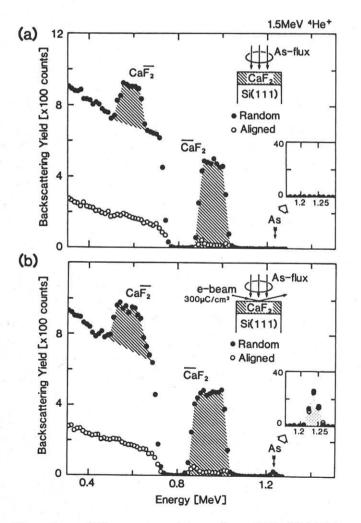


Fig. 1 RBS spectra taken from $CaF_2/Si(111)$ structures, in which (a) is only As-impinged and (b) is As-impinged during e-beam exposure.

the sample in the Fig. 1(b) was exposed to an e-beam to a dose of $300\mu\text{C/cm}^2$. It is clear that numbers of As atoms are adsorbed on the surface of the e-beam-exposed CaF_2 in Fig. 1(b), while they are not adsorbed on the unexposed CaF_2 surface.

Thermal stability of these As atoms adsorbed on the CaF, surface is examined. Figure 2 shows the changes of As signals in the aligned RBS spectra of the As-adsorbed CaFo/Si(111) structure by annealing at various temperatures in N2 atmosphere. Almost no channeling effect was observed for the As spectra in this figure, which means that the counts of As signals correspond to the total adsorbed atoms. The amount of As atoms corresponding to about 3 monolayers before annealing decreases largely to be 1.7 monolayers when the sample is annealed at 550°C for 10min. This large desorption of As atoms is speculated, at present, to be due to the removal of As atoms which are located in the interstitial state or arround the Ca clusters. In this speculation, that is, a part of As atoms around the Ca cluster, generated by e-beam exposure with an excess energy^{3,5)} of 3keV, come off the surface together with the Ca clusters by annealing at 550°C.

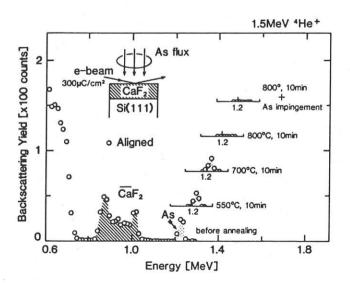


Fig. 2 Change of the aligned As signals of the As-adsorbed $CaF_2/Si(111)$ structure by annealing at various temperatures.

It is noteworthy that no significant change could be observed in the adsorbed As atoms from 550°C to 700°C. Souda and Aono reported⁶⁾ that the CaF₂ surface exposed to e-beam under vacuum condition was restored to the initial surface, which had existed before e-beam exposure, by annealing at 500°C. In our experiment, however, the As-adsorbed CaF₂ surface was stable up to 700°C and no more As atoms were desorbed from the surface of CaF₂ film, which suggests that As atoms are strongly sticked on the CaF₂ surface, e.g. As atoms are substituted for fluorine (F) atoms by e-beam exposure under As impingement.

When the sample was further annealed at 800°C for 10min, As atoms disappeared from the surface of CaF₂ film. And once As atoms were desorbed from the surface of CaF₂, we could not observed them even though the sample were impinged again by an As₄ flux. This fact indicates that the surface of the e-beam exposed CaF₂ film is completely restored to the initial state by annealing at 800°C. Annealing in the vacuum condition also gave the similiar results as in the above N₂ atmosphere.

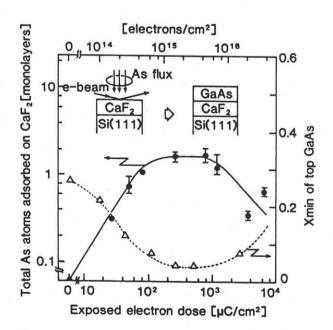
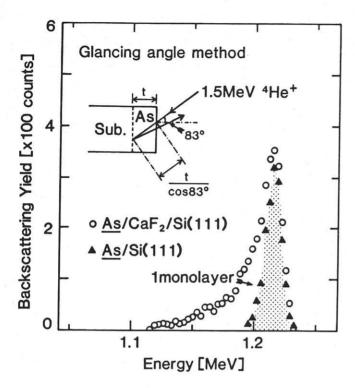


Fig. 3 electron dose vs. the amount of the As atoms adsorbed on the CaF2 surface, and electron dose vs. χ_{min} of top GaAs films.

Figure 3 shows the electron dose vs. the amount of As atoms adsorbed on the CaF, surface which was annealed at 550°C for 10min. This annealing condition was best for the growth of GaAs overlayer. 3) In the low dose region, the amount of As atoms increases almost linearly with increasing the dose to about 100μC/cm². As the e-beam exposure further proceeds, the amount shows a saturated tendency in the dose range between 100µC/cm² and 1mC/cm². Finally, the adsorbed As atoms decrease with the dose in the region higher than 1mC/cm². It is interesting to note that the crystalline quality of top GaAs films, grown on the As-adsorbed CaF, surface, has a strong correlation with the amount of the adsorbed As atoms on the CaF2 surface. In the saturation region, the amount of adsorbed As atoms corresponds to about 1.7 monolayer. This value indicates that As atoms do not exist only in the uppermost F sites, but they also exist in bulk CaF2. Thus, the distribution of the excess As atoms is investigated using a glancing angle RBS method.

Figure 4 shows the random spectrum for As atoms in the e-beam-exposed CaF₂/Si(111) structure. The electron dose to the sample was 300µC/cm². As signal from an As-adsorbed Si(111) substrate, which was obtained by impinging an As_{L} flux at 700° C to Si(111) (7×7) surface, is also shown as a reference. In the reference sample, it has been reported that As atoms of 1 monolayer are adsorbed uniformly. 7-8) It is found from this figure that As atoms in the CaF2/Si(111) structure are distributed to about 10nm in depth from the surface by exposure of a 3keV e-beam. It is also found from comparison with a reference sample that the As atom profile is composed of a surface peak and a penetrating tail, and that surface peak area of adsorbed As atoms corresponds to the amount of a monolayer or a little less. Therefore, the excess As atoms beyond 1 monolayer, referred in Fig.



Random As signal of the As-adsorbed CaF2/Si(111) structure measured by glancing angle method in RBS. The incidence of 1.5MeV 4 He $^+$ ions is tilted by 83° against the <111> normal axis of the sample. As signal of Si (111) substrate, on which As atoms of 1 monolayer are adsorbed, are also shown as a reference.

3, can be explained from the depth distribution of As atoms.

§4. Conclusion

In order to explain the growth mechanism of the EBE-epitaxy, we investigated the CaF surface modified by e-beam exposure under As impingement. Main results obtained are as follows.

- 1) As atoms are adsorbed on the CaF_2 surface exposed to e-beam under As impingement while they are not adsorbed on the unexposed surface. The As-adsorbed CaF, surface is thermally stable up to 700°C.
- The quality of top GaAs films is strongly dependent on the amount of As atoms adsorbed on CaF, films.

3) When e-beam exposure to the CaF, surface is carried out with an energy of 3keV, As atoms are penetrated to 10nm in depth from the surface of CaF, film. As atoms estimated at nearly 1 monolayer or less are adsorbed on the uppermost layer of CaF, film.

According to the above results and the $reports^{6,9)}$ that the uppermost F atoms of CaF, are dissociated by e-beam exposure, we can conclude that uppermost As atoms of modified CaF, film, at least, contribute to the improvement of the quality of top GaAs films.

Acknowledgement

This work is supported by a 1987 Grant-in-Aid for Special Distinguished Research (No. 59060002) from the Ministry of Education, Science and Culture of Japan.

Reference

- 1. T. Asano, H. Ishiwara, H. C. Lee, K. Tsutsui and S. Furukawa: Jpn. J. Appl. Phys. 25 (1986) L139.
- 2. H. C. Lee, T. Asano, H. Ishiwara and S. Furukawa: Jpn. J. Appl. Phys. 25 (1986)
- 3. H. C. Lee, H. Ishiwara, S. Kanemaru and S. Furukawa: Jpn. J. Appl. Phys. <u>26</u> (1987) L1834.
- 4. H. C. Lee, T. Asano, H. Ishiwara, S. Kanemaru and S. Furukawa: Extended Abstracts of 19th Conf. Solid State Devices and Materials, Tokyo, 1987, p. 163. 5. H. C. Lee, T. Asano, H. Ishiwara and

S. Furukawa: submitted to Jpn. J. Appl. Phys.

- 6. R. Souda and M. Aono: to be published in Proc. of the Int. Conf. Structure of Surfaces (Amsterdam, 1987). 7. R. I. G. Uhrberg, R. D. Bringans,
- M. A. Olmstead, R. Z. Bachrach, and J. E. Northrup: Phys. Rev. <u>B35</u> (1987) 3945.
- 8. R. S. Becker, B. S. Swartzentruber, J. S. Vickers, M. S. Hybertsen, and S. G. Louie: Phys. Rev. Lett. <u>60</u> (1988)
- 9. K. Saiki, Y. Sato, K. Ando and A. Koma: Surface Science, 192 (1987) 1.