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Atomic Layer Modification by Low Energy Electron Beam to Control the GaAs/CaF_2 Heterointerface

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Surface modifications of epitaxial CaF_2 on Si(111) by a low energy electron beam in order to get modified surfaces with reduced damage on which high quality GaAs films could be grown were studied. By using the X-ray photoelectron spectroscopy (XPS) measurements, it has been found that surface modification where F atoms are replaced by As atoms can be confined to nearly one monolayer of the top surface of CaF_2(111) by an using electron beam of which energy is as low as near threshold value to make the modification.

1. Introduction

The electron beam exposure and epitaxy (EBE-epitaxy) method [1] is a successful method to grow the heterostructure of GaAs on CaF_2, by which SOI (semiconductor-on-insulator) structures on Si substrates could be realized for many attractive future applications.

In this method, the surface layer of CaF_2(111) is irradiated by an electron beam with an As_4 molecular beam to replace the surface F atoms by the As atoms before GaAs growth. As a result of this process, the wettability of GaAs on the CaF_2 surface is improved so that good crystallinity of GaAs film can be obtained.

However, the actual interface of the GaAs/CaF_2 might have been degraded because of irradiation damage caused by deep penetration of high energy (3keV) electrons which have been used so far. It is necessary to replace the atoms only in the top layer and to remain no damage under the layer. Consulting binding energy of F-Ca in CaF_2, the energy for desorption of F is considered to be lower than several 10eV. Therefore, such a low energy electron is expected to be useful to obtain the atomic layer modification.

In this work, the effect of surface modification of CaF_2 by a low-energy electron beam was investigated and a possibility of the atomic layer modification was indicated.

2. Experimental

The experiments were carried out in a three-chambers MBE system. After CaF_2 films were grown on Si(111) substrates by MBE, their surfaces were exposed to low energy (0-305eV) electron beams at a dose of 3000 μC/cm^2 under simultaneous impingement of an As_4 molecular beam in-situ. The low energy electron beam was generated by a tungsten filament and irradiated on the biased substrate whose temperature was kept at 300° C to avoid the charging up of CaF_2. The dose of an electron beam was roughly estimated by measuring the current flow into the substrate holder.

After that, the samples were transferred to the analysis chamber keeping high vacuum and XPS measurements were performed using AlK α X-ray to examine the amount of As atoms and their binding states. Intensity from 1 monolayer(ML)-As was calibrated by a reference sample of 1ML-As adsorbed on Si(111) prepared by the reported method [2].

3. Results and discussion

Figure 1 shows the XPS spectra of As(2p3/2) from the surface of CaF_2. Both samples were prepared under impingement of As_4 flux at 300° C, one of which shown as (a) had been exposed to 305eV electron beam. As(2p3/2) signal could be observed only in the electron beam exposed sample. The spectrum shown by the dashed line in the Fig.1(a) is that obtained from the As(1ML)/Si(111) reference sample. It is noted that the surface of CaF_2 irradiated by the electron beam has been modified by 1 ML-As layer.

The same measurements were carried out by using

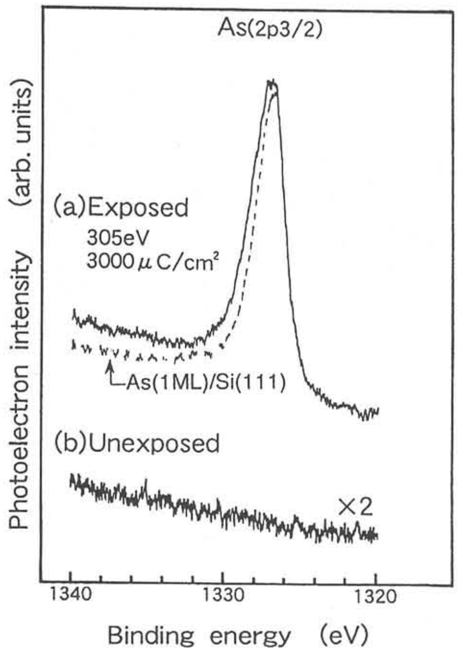

Fig.1 XPS spectra of As(2p3/2) on the CaF_2. (a):irradiated by electron beam (305eV). (b):unirradiated by electron beam. Both samples were irradiated by As_4 molecular beam.

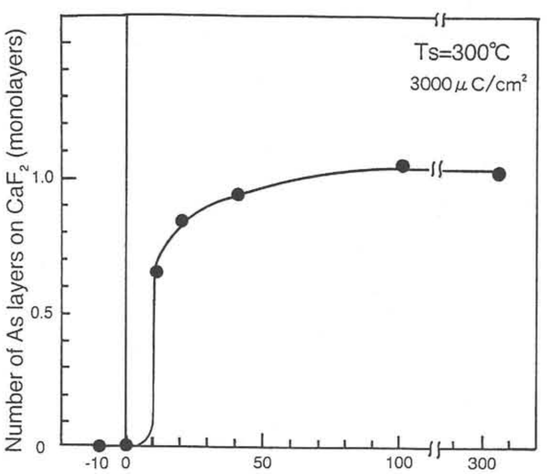

Fig.2 The relation between the electron beam energy and the number of As layers on $CaF_2(111)$.

lower energy. Figure 2 shows the relation between the amount of As on the $CaF_2(111)$ and electron beam energy. The adsorption of As on the CaF_2 is found to occur when the electron beam energy exceeds 10eV and to decrease drastically below 10eV. Therefore, it can be said that the minimum energy to modify the $CaF_2(111)$ surface electronically is around 10eV. This value is considered to be reasonable by referring other reports [3][4][5].

Figure 3 shows the change of the XPS spectra of As(2p3/2) from CaF_2 due to annealing treatments. These samples were irradiated by the electron beam of 40eV or 305eV. Before annealing treatments, spectra for both samples showed a single peak shape and the amount of As at the surface is nearly 1ML.

In the case of use of the 305eV beam, the spectrum changed drastically after annealing at 400° C for 10min. The chemical shift to the higher binding energy can be observed. And the sum of intensities of both two peaks decreases as the annealing temperature becomes higher. Since O(1s) peak was not observed even after these annealing, it can be said that arsenic oxide has not been formed. Therefore, these spectral changes indicate that some As atoms have desorbed and the rest As atoms have diffused into the CaF_2 during the annealing.

In the case of use of the 40eV beam, on the contrary, no chemical shift of As(2p3/2) can be observed even after the annealing at 550° C. Only the decrease of peak intensity can be observed. If we assume that the origin of the chemical shift is the damage of CaF_2 into which the As can be diffuse easily, it can be said that 40eV electron beam causes very small irradiation damage and that the monolayer surface modification of CaF_2 could be performed by using such a "low energy" electron beam.

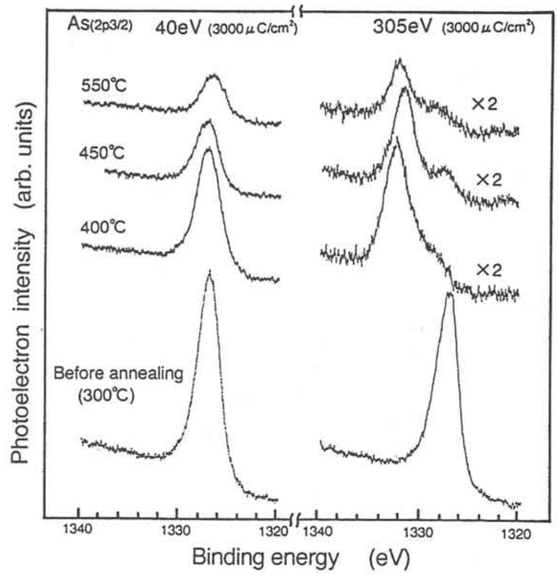

Fig.3 The changes of XPS spectra of As(2p3/2) on the CaF_2 depending on annealing temperature. The samples were irradiated by electron beam of 40eV or 305eV.

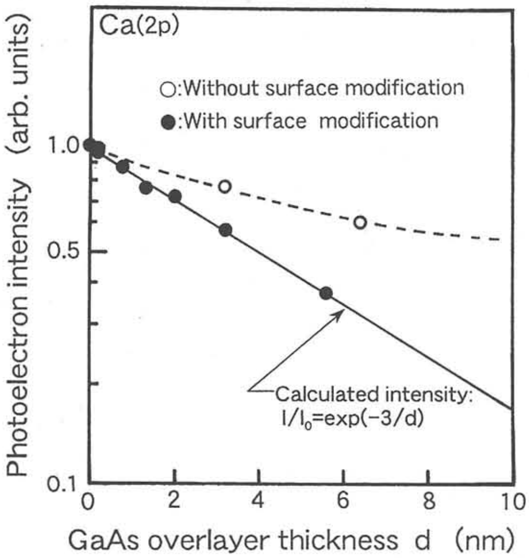

Fig.4 Normalized XPS signal intensities of Ca(2p3/2) as a function of GaAs overlayer thickness. ● and ○ show for the sample irradiated by electron beam of 40eV and unirradiated by electron beam before the growth of GaAs overlayer, respectively.

The initial stage of growth of GaAs on the modified surface of CaF_2 was also studied by using XPS. Figure 4 shows the relation between photoelectron intensity from CaFs and the thickness of GaAs overlayer, where the intensities are normalized by initial value before GaAs growth. It is found for the sample which was exposed to the electron beam of 40eV that the intensity of Ca(2p) is decreased exponentially as increased the thickness of GaAs overlayer. The solid curve in Fig.4 has been calculated by assuming that the escape depth from GaAs, λ, is 3nm. The experiment agrees with the calculation well. This indicates that GaAs is grown two-dimensionally. On the other hand, the intensity of Ca(2p) is not found to be so much decreased exponentially for the sample which was not exposed to electron beam, in which GaAs might be grow with island formation. Figure 5 shows surface morphology of the overgrown GaAs after 70nm growth. GaAs grown on the surface modified by the electron beam shows very smooth surface.

These results show that GaAs can grow two-dimensionally on the modified surface after a few monolayers growth. This is indicating that the modified CaF_2 surface should be filled with As atoms. Combining the result that the amount of As adsorbed by the electron beam exposure is 1ML, it can be said that almost all of these As atoms should be in the top layer of CaF_2.

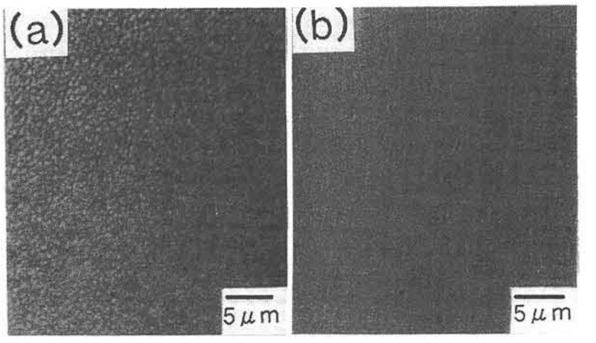

Fig.5 Surface morphology of GaAs layers on CaF_2(111). (a): unirradiated by electron beam. (b):irradiated by 40eV electron beam before GaAs growth.

4. Conclusion

Only around 10eV is sufficient to modify the surface of CaF_2/Si(111). Behavior of adsorbed As and the two-dimensional growth mode of GaAs grown on the modified CaF_2 surface indicate that the monolayer modification with small irradiation damage of CaF_2 has been realized by using electron beam of near threshold energy, 40eV.

Acknowledgment

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