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Sm^{2+} Photoluminescence and X-ray Scattering Studies of A-and B-Type Epitaxial CaF_2 Layers on Si(111)

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Bivalent samarium photoluminescence and X-ray crystal truncation rod scattering have been studied to characterize CaF_2/Si(111) structures with the interface region (two CaF_2 monolayers) grown at low (200 °C) and high (770 °C) temperatures. It was found that growth temperature of initial two monolayers determines not only the type of epitaxy (A or B) but also strain relaxation, defect concentration and Ca-Si interlayer spacing at the interface.

1. INTRODUCTION

Besides considerable interest to CaF_2 epitaxial layers due to their promising various important applications in microelectronics, CaF_2/Si(111) structures became a model object for studies of crystalline insulator-semiconductor interface [1,2]. Recently new intriguing information about the atomic structure of the interface has been obtained [3]. The most studies were concentrated, however, on high temperature grown structures having type-B epitaxial relations between the CaF_2 layer and Si substrate where the layer is rotated by 180° around surface normal to the substrate. Low temperature growth results in type-A (non-rotated) epitaxial structures [4] which have attractively low density of the interface states [5] and are expected to have less density of the interfacial defects. For many applications thin (15-30 nm) insulating layers are desired. In this study, a sensitive technique of impurity photoluminescence probe [6] has been applied for characterization of crystalline quality and measuring of elastic strain in thin type-A and type-B epitaxial layers. Atomic arrangement s at the CaF_2 /Si(111) interface have been analyzed by technique of X-ray crystal truncation rod (CTR) scattering [7,8].

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2. EXPERIMENTAL

The structures for this study have been grown in the MBE system described in Ref. [4]. After standard Shiraki chemical cleaning, silicon substrates were placed into the growth chamber where they were heated at 900 °C during 30 min to get distinct 7x7 Si(111) superstructure in reflection electron diffraction pattern. The molecular cell for CaF_2 deposition was loaded by pieces of pure or Sm-doped (0.3 mol.%) fluorite. The deposition rate was about 1 nm/min.

For measurements of Sm^{2+} ion PL spectra the samples were placed into a helium cryostat. The sample temperature was 1.7K or around 30K. The He-Ne laser (λ=633nm) has been used to excite PL. The spectra were registered using a grating monochromator, a multialkaline photo-multiplier and a lock-in amplifier operating at 1.8 kHz or photon counting system.

X-ray measurements have been carried out at the Photon Factory (KEK, Tsukuba) using beamline BL-6A_2 and Weissenberg camera with imaging plate as a detector.

3. RESULTS AND DISCUSSION

As it was demonstrated in Ref. [6], bright photoluminescence (PL) produced by $4f^5 5d \rightarrow 4f^6$ electron transitions in Sm^{2+} ion can be used for measurement of the elastic strain of epitaxial fluorite films and for the characterization of their crystalline quality. Figure 1 shows PL spectra of two CaF_2:Sm^{2+} layers of 15nm thick, which type-B interfaces with Si(111) substrate were formed at 770°C but the films were grown at 200° C (curve (a)) and 770 °C (curves (b)). The dashed curve refers to bulk CaF_2:Sm^{2+} crystal.

The lattice constant of the fluorite at low temperatures is larger than that of Si about 0.3%. Therefore compressive strain of that value as was observed in curve (a) indicates pseudomorphic (coherent) growth mode of this film. Relatively narrow Sm^{2+} emission of the film confirms this conclusion. On the other hand PL spectrum of CaF_2 layer grown completely at high temperature (curve b) shows large tensile film strain (~1.3 %) and broader emission line. The difference between these two spectra is due to the breakdown of the pseudomorphic growth mode and larger thermal expansion coefficient of CaF_2 compared with Si.

Figure 1(c) shows PL spectrum of Sm^{2+} ions in 10 nm thick CaF_2 layer grown at 200 °C. Such growth conditions result in type-A epitaxial relation between Si substrate and fluorite layer [4]. Relatively broad emission line in this CaF_2 layer indicates large random component of the strain which is due to high concentration of structural defects. The average strain in this film (-0.3%) is different from the value for coherent film. It shows that type-A film is relaxed. The relaxation can be due to different bonding at type-A interface as well as structural defects originating from not complete removing of 7x7 Si(111) superstructure at low growth temperature.

The effect of annealing type-A structures is seen in Fig.2 where (a) corresponds to as-grown layer. The epitaxial relation remains the same but spectral position of the emission line and corresponding strain in CaF_2 is found to depend on the temperature of the annealing. For structures annealed during 30 min at 400, 500 and 600 °C, the tensile strains in the plane of the interface were about 0.3, 0.65 and 1.0% correspondingly (Fig.2, (b-d)). Such dependence of the fluorite film strain on the annealing temperature shows that it is mainly due to larger thermal expansion coefficient of CaF_2 than that of Si. One can observe noticeable decrease of the PL line width in the structure annealed at 500 and 600 °C (Fig.2, (c),(d)). It shows the better crystalline quality of the annealed films.

The CTR scattering is a rod shaped X-ray scattering emanating along the surface normal direction from each Bragg point, due to truncation of the periodic lattice at the surface or interface. The intensity profile along the rod is extremely sensitive to the lattice termination such as surface or interface roughness, lattice relaxation and an existence of epitaxial layer on the surface so that its analysis provides detailed information about these parameters [7,8].

In X-ray diffraction patterns obtained from 9 monolayer thick CaF_2 layers grown at the same temperature 200 °C but with different temperature of the interface formation (200 °C and 770 °C) , positions of 113 CaF_2 Bragg peak in these structures indicated type-A epitaxial relation for low and type-B for high temperature of the interface formation. The integrated intensity along crystal

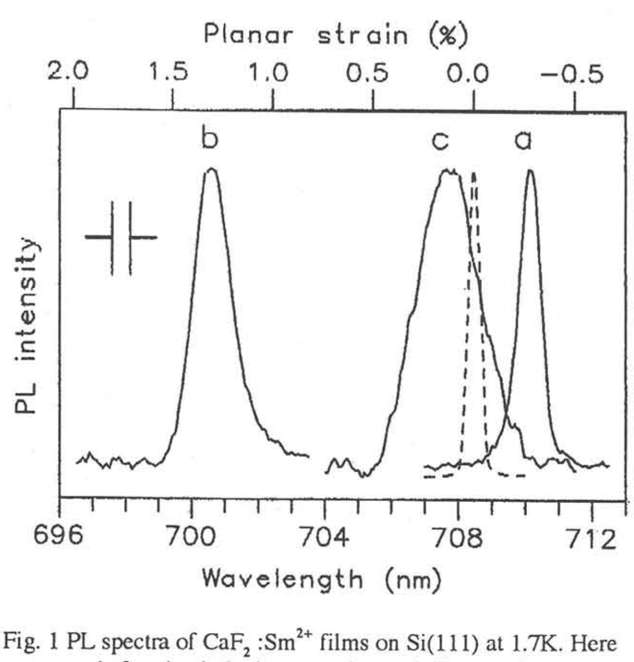

Fig. 1 PL spectra of CaF_2 :Sm^{2+} films on Si(111) at 1.7K. Here and after the dashed curve refers to bulk crystal.

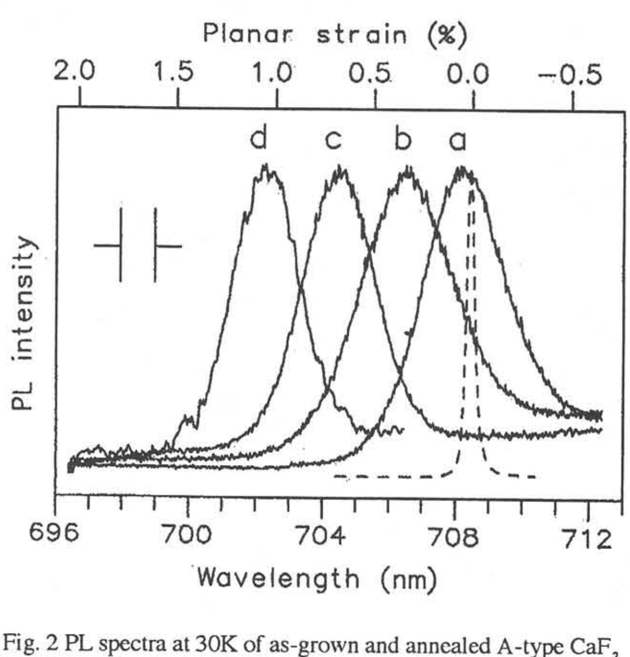

Fig. 2 PL spectra at 30K of as-grown and annealed A-type CaF_2 :Sm^{2+} films of 6nm thick.

truncation rod scattering near the 111 Bragg point obtained for these two structures by subtracting the background are shown in Fig.3 and 4 correspondingly. Sharp peaks at k_z =1.0 correspond to 111 Bragg scattering from Si substrate and wings are mainly due to the scattering from CaF_2 layer. The solid curves were obtained using the simplest model for CTR scattering [8] and taking the PL data on CaF_2 strain into account.

From the data presented in Fig.3 it was found that normalized distance at the interface between the last silicon diffracting plane and the first Ca plane is d/a_0= 1.2±0.05 where a_0 is interlayer spacing between (111) Si planes. The interface spacing for this A- type structure could be explained by an influence of 7x7 Si(111) superstructure which is expected to be more stable at low growth temperature. The parameter of crystalline quality (occupation factor) of the fluorite layer is relatively low, Q=0.4, but it is consistent with broad line in PL spectra in Fig.1(c).

The best fit between simulated and experimental intensity profiles for type-B structure was obtained for d/a_0= 1.46±0.02 (Fig.4). Very close value was found in Ref. [3] where it was explained by two layers CaF-CaF interface between CaF_2 and Si(111). The origin of such complicated interface structure is not so clear yet and further study is needed. From fitting procedure it was also obtained high value of the film crystalline quality parameter, Q=0.9. It correlates with narrow emission line in PL spectrum in Fig.1(a).

4. CONCLUSION

To summarize, CaF_2 /Si(111) structures with type-A and type-B epitaxial relations have been characterized by techniques of rare-earth ion photoluminescent probe and X-ray crystal truncation rod scattering. It was shown that the fluorite film strain for the as-grown A- type structure is different from those typical for type-B. It was supposed that not so good crystalline quality of the as-grown A- type structure can be connected with 7x7 superstructure which is more stable at lower temperatures. From the analysis of the crystal truncation rod scattering different spacing at the interface for type-A and type-B structures have been found.

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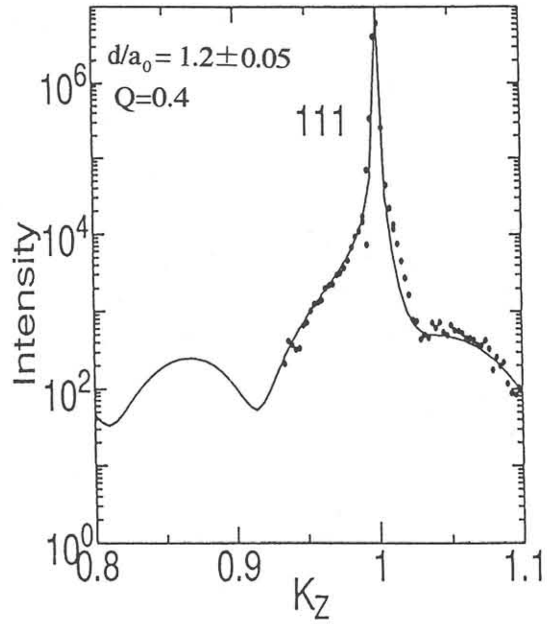

Fig. 3 The integrated intensity of A-type CaF_2/Si along CTR scattering near the 111 Bragg point.

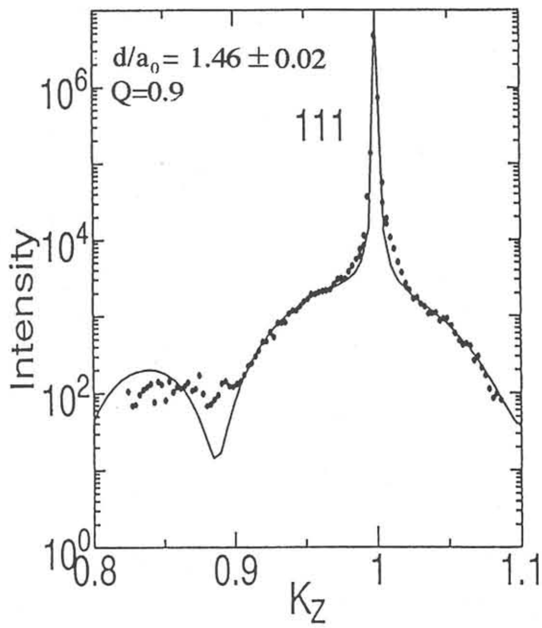

Fig. 4 The integrated intensity of B-type CaF_2/Si along CTR scattering near the 111 Bragg point.