EPITAXIAL RELATIONS IN BaF_2 FILMS GROWN BY MBE ON Si(111) SUBSTRATES

A.Belenchuk, A.Fedorov*, V.Zenchenko, V.Lukash, A.Vasilyev
Institute of Applied Physics, Kishinev, 277028, Moldova
**Institute of Device Technology, Kharkov, Ukraine*

SUMMARY

The dependence of the epitaxial orientations of the films in BaF_2/Si(111) heterostructures on growth conditions and the influence of heat treatment on the stability of epitaxial relations in such structures are investigated. The correlations between the types of epitaxial relations and structures of interface are also discussed.

1. INTRODUCTION

On a (111) oriented silicon substrates the fluoride films grow in two distinct epitaxial orientations. The films have orientation either identical to those of the substrate (A-type relation), or their structure is rotated respectively to the substrate by 180^0 about the surface normal [111] axis (B-type relation). The CaF_2 films grown by conventional MBE method (growth temperature T_g and growth rate V_g are the constants during the whole deposition process) prefer to have B-type orientation, whereas in SrF_2 and BaF_2 films grown under the same growth conditions a polydomain (A+B)-type orientation is observed [1]. It was expected that A-type provides a maximum structural perfection of fluoride films on Si(111) substrates [2]. Recently it was shown that a two step growth method allows to obtain uniform A-type CaF_2 [3] and BaF_2 [4] films on Si(111).

In this paper, we have studied the epitaxial relations in BaF_2/ Si(111) heterostructures and their dependence on growth an annealing conditions.

2. EXPERIMENTAL PROCEDURE

The BaF_2 films were deposited in an ultrahigh vacuum (UHV) system with a base pressure of about 10^{-8} Pa. The UHV system was equiped with a high energy electron difractometer (RHEED) and Auger-electron spectrometer.The n- and p- type conductivity Si(111) wafers were used as the substrates.

Three different methods were used for the BaF_2 films deposition : conventional MBE method (T_g= 500°C, V_G= 0.1 nm/s), as well as low and high temperature (LT & HT) two step methods. In the latter case a thin buffer layers (2-40 nm) were first grown at T_i = 150°C and T_i = 850°C for LT and HT two step methods, respectively. The LT buffer layers were annealed at 700°C for 50 s. The succeeding BaF_2 layers of about 300nm thick were grown under ordinary growth conditions (T_g =500°C , V_g = 0.1 nm/s).

Same specimens were annealed at different temperatures between 700 and 850°C for 10 min. To avoid a large tensile stress in the films resulted from a large discrepancy in thermal expansion coefficients between BaF_2 and Si , a cooling rate did not exceed 10 °C/min.

0-7803-2647-4/95/$4.00 © 1995 IEEE

The epitaxial orientation of BaF_2 films and their structural perfection (a full-width at half maximum of rocking curves δ) were characterized by double crystal X-ray diffraction with the use of CuK_α radiation and Si(100) monochromator. The thickness of the BaF_2 films d were determined by ellipsometry.

3. RESULTS AND DISCUSSION

Analisys of buffer layers by RHEED showed that growth under low temperature leads to microroughness of the surface and bad crystallinity which are confirmed by RHEED patterns from these layers (see Fig. 1a). The annealing of buffer layers gives atomicaly flat surface and excellent crystallinity of the films (see Fig. 1b).

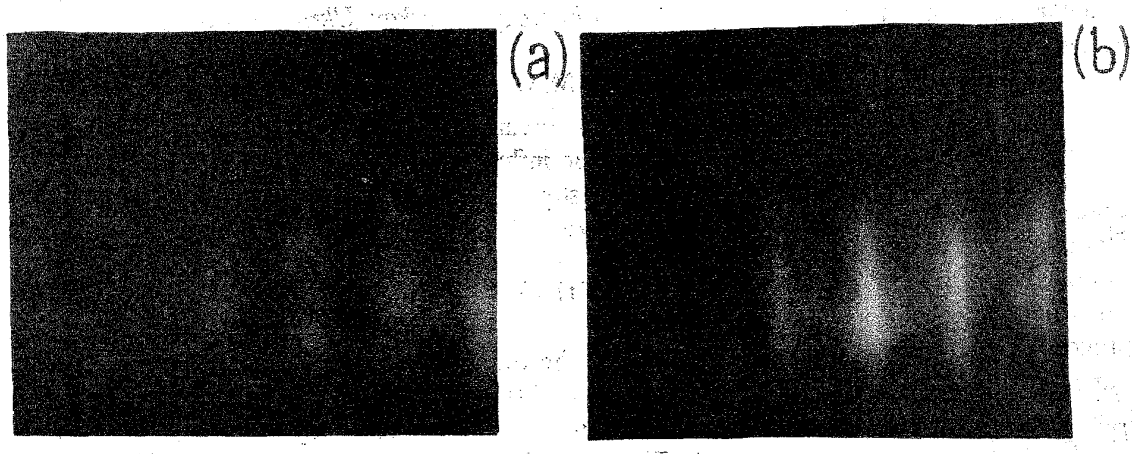


Fig. 1. RHEED patterns from BaF_2/Si(111) structure grown at T_g=150°C (a), and annealed at T=750°C for 50 s (b).

Some structural characteristics of BaF_2 films obtained from X-ray diffraction data analysis are listed in Table.

Table

N	Growth method	Annealing conditions	Epitaxial relations	$V_B/(V_A+V_B)$	δ^0	d, nm
1	1 step		A+B	0.87	0.37	310
2	1 step	750°C, 10min	A	0.00	0.28	310
3	1 step	850°C, 10min	A	0.00	0.30	290
4	LT 2 step		A	0.00	0.34	300
5	LT 2 step	750°C, 10min	A	0.00	0.25	300
6	LT 2 step	850°C, 10min	A	0.00	0.29	280
7	HT 2 step		A+B	0.55	0.33	310

As it follows from this table , the epitaxial relations in BaF_2 films are determined by the growth conditions . The specimen grown by conventional one step method had polydomain (A+B)-type relation. The total volume of A-type domains V_A was about 13%. This result is in well agreement with the results of papers [1,5], where it was established that this quantity can reach 25% depending on the growth temperature.

The LT two step method resulted in uniform A-type orientation of BaF_2 films. Whereas in the specimen grown by HT two step method the polydomain (A+B)-type state was observed. The total volume of A-domains in this case was about 45%.

According to the assumption of Ohmi et al. [3], A-type orientation of CaF_2 films is a metastable state. In order to investigate this question in the case of BaF_2 films we have considered the influence of post growth annealing upon the epitaxial relations in BaF_2/Si(111) structures. It was established that the polydomain (A+B)-type state in the specimens, obtained by one step growth method, is transformed into uniform A-type state during the heat treatment at 750°C for 10min. The A-type state was not changed even when the annealing temperature was risen up to 850°C. At this temperature, however , some degradation of crystalline quality and partially reevaporetion of BaF_2 films were observed. From these results, we can conclude that A-type epitaxial relation in BaF_2 /Si(111) heterostructures is stable at least up to 850°C.

The type of epitaxial relation of fluoride films is determined by a sign of quantity $f = f_A - f_B$, where f_A and f_B are free energy per unit area of interface with A-and B-type orientations of the films, respectively. In monodomain state one of the following conditions must be fulfilled : $f_A << f_B$ (A-type) either $f_B << f_A$ (B-type). The polydomain states in the films may be caused by both energetic and kinematic reasons . The change of the free energy of the film in polydomain state F_{pd} one can describe by a following equation:

$$F_{pd} = f_A S_A + f_B S_B + f_{A\text{-}B} S_{A\text{-}B} \quad , \qquad (1)$$

where S_A and S_B are the areas of interface with A- and B-type domain , respectively; $f_{A\text{-}B}$ is the free energy per unit area of boundary between A- and B-type domains; $S_{A\text{-}B}$ is the area of these boundaries. The contribution to F_{pd} from boundaries is proportional to the thickness of the film. This means that in thin films the polydomain state will be observed when $f_A \sim f_B$. For thick films the last term in Eq.(1) makes the polydomain state unfavourable. However, the polydomain state can be observed even in this case when the mobility of A-B boundaries is low or they are pinned at structural imperfections of the films.

It is known that the growth of IIa fluorides at lowered temperature (T_g <600°C) leads to the formation of a nearly stoichiometric structure of fluorine films at the interface, which can be described by the following formula Si-Si-$(F\text{-}M\text{-}F)_n$ [6], where M is an atom of IIa group. Such structure of interface results in polydomain (A+B)-type orientation of BaF_2 films. During the annealling of BaF_2/Si(111) structures the fluorine atoms from interface monolayer can redistributed in the vicinity of interface. A cluster calculation of the energy of fluorine atom at the (111) silicon surface [7] has shown that it has several stable positions both at the silicon surface and beneath surface between second and third layers of silicon atoms. It should be noted that the fluorine atoms distribution in the vicinity of interface has a greatly effect on the values of energy densities f_A and f_B [8]. We assume that nonstoichiometric structure of interface with fluorine atoms localized beneath silicon surface results in A-type orientation of BaF_2 film.

The high temperature growth of Ca and Sr fluorides on Si(111) leads to the formation of nonstoichiometric structure of interface. Such structure can be described by the following formula Si-Si-M-F-(F-M-F)$_n$ and it gives the B-type orientation of CaF_2 and SrF_2 films [9,10]. The main distinction between interfaces obtained by LT and HT two step method consists in the present or absent of the fluorine atoms beneath silicon surface.

In the contrary to Ca and Sr fluorides, the BaF_2 film grown on Si(111) by HT two step method had (A+B)-type of epitaxial relation. The reason of such different behaviour is now under consideration.

4. CONCLUSION

The investigation to be curried out shown that the epitaxial relations in BaF_2 /Si(111) heterostructures are determined by the structure of interface, which is very sensitive to both growth and annealing conditions. It was established that polydomain (A+B)-type state in the films grown by conventional MBE method is unstable and is transformed into uniform A-type state during post-growth annealing. A-type state is stable up to 850°C. The HT two step method results in polydomain (A+B)-type orientations of BaF_2 films.

REFERENCES

1. T.Asano, H.Ishiwara, Appl. Phys.Lett. **42**, 517 (1983).
2. L.Schowalter, R.Fatauer, F.Ponce, et.al., Mater.Res.Soc. Symp. Proc., **67**, 125 (1986)
3. S.Ohmi, K.Tsutsui, S.Furukawa, Jpn.J.Appl.Phys., **33**, 1121 (1994)
4. A.Belenchuk, A.Fedorov, V.Lukash, et. al., Mater.Res.Soc.Symp. Proc., **356** (1994), in press.
5. H.Zogg, M.Huppi, P.Maier, R.Knobel, Helv. Phys. Act, **59**, 164 (1986).
6. F.Himpsel, F.Hillebrecht, et al. Appl.Phys.Lett., **48**, 586 (1986).
7. M.Seel, P.Bagus, Phys. Rev.**B23**, 2023 (1983).
8. K.Path, A.Anderson, Phys.Rev **B38**, 8264 (1988).
9. R.Tromp, M.Reuter, Phys.Rev.Lett., **61**, 1756 (1988).
10. M.Olmstead, R.Bringans, Phys.Rev. **B41**, 8420 (1990).