A — 6 — 4 Lattice-Matched Epitaxial Growth of Semiconductor Films onto Insulator(Mixed Fluoride) /Si Structures

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Semiconductor/insulator heteroepitaxial structures stacked onto Si substrates are very attractive for such three-dimensional devices as the high speed LSI's, the optoelectronic devices, and the integrated sensors, as well as for substituting expensive bulk semiconductor substrates. However, if conventional crystalline insulators such as Al_2O_3 and $MgO{\cdot}Al_2O_3$ are used in this structure, it is generally impossible to match the lattice constants between the semiconductor and insulator films. In that case, we may not use this structure for the high speed or optoelectronic devices, since the crystalline quality of the films is seriously degraded by the lattice mismatch. In this paper, a novel lattice-matched epitaxy of the semiconductor/insulator structures by use of mixed group II-a fluorides is presented. Group II-a fluorides such as CaF_2, SrF_2 and BaF_2 crystallize in the cubic fluorite (CaF_2) structure, which is closely related to the diamond, cubic ZnS, and NaCl structures. The structure is also related to the hexagonal structures on particular planes like (111). The lattice constants of the fluorides and typical semiconductors are summarized in Fig.1. Since the lattice constant of the mixed fluorides changes linearly with the mixing ratio[1], we can see from Fig.1 that the constant of the fluorides is exactly or closely matched with that of most interesting semiconductors. So far, the epitaxial growth of the fluoride films has been reported only for BaF_2 on InP and CdTe[2], and CaF_2 on Si[3,4]. Therefore, we set up the following experiments in this study; (1) the growth of SrF_2 and BaF_2 films onto Si substrates, (2) the growth of mixed $Ca_{1-x}Sr_xF_2$ films onto Si substrates, and (3) the growth of Ge films onto the fluoride/Si structure.

In the first experiment, chemically cleaned n-type Si(111) wafers with resistivity of ∿10 Ωcm were loaded in a vacuum chamber with a base pressure lower than 1×10^{-6} Pa. SrF_2 and BaF_2 grains with 99.99 % purity were evaporated from a Ta boat onto the Si substrates kept at temperatures from 400 to 800°C. The crystalline quality and the composition ratio of the deposited films were analyzed by Rutherford backscattering spectroscopy (RBS) and transmission electron microscopy (TEM). Figure 2 shows typical RBS spectra for a BaF_2 film on a Si(111) substrate. As can be seen from this figure, the stoichiometry and crystalline quality of the film is almost perfect, as long as they are measured by RBS. The excellent films were obtained at substrate temperatures ranging from 500 to 600°C. Similarly, the excellent films were obtained for SrF_2 at 600°C. From these results, as well as the previous results for CaF_2 films[3,4], we conclude that the group II-a fluorides grow epitaxially onto Si(111) substrates and that the quality is not seriously degraded in spite of the large lattice mismatch (about 14 % for BaF_2 on Si).

Next, epitaxial growth of the mixed $Ca_{1-x}Sr_xF_2$ films onto Si substrates and the growth of Ge films onto the $Ca_{1-x}Sr_xF_2$/Si structure were investigated. In this experiment, mixed powder of CaF_2

and SrF_2 was evaporated from a single Ta boat onto Si(111) substrates kept at temperatures from 500 to 900°C. In the formation of the double-heterostructure, Ge was evaporated from a 2 kw e-gun onto the fluoride film without breaking the vacuum. The samples were kept at temperatures ranging from 400 to 600°C during deposition. It was found from RBS that the mixing ratio of the fluoride films was rather uniform at any depth and that the crystalline quality of the films depended on the mixing ratio as well as the substrate temperature. At present, the channeling minimum yield in RBS is about 10 % for the best quality film, which is about three times higher than the expected perfect crystal value. Ge films were then grown onto the best quality $Ca_{1-x}Sr_xF_2$ films. Typical RBS spectra for the $Ge/Ca_{0.6}Sr_{0.4}F_2/Si$ structure are shown in Fig.3. From this figure, we can say that (1) the Ge film grows epitaxially onto the mixed fluoride film and (2) the crystalline quality of the Ge film is much better near the interface with the fluoride film than the quality of the film directly grown onto the Si substrate[5]. The better quality is considered due to the smaller lattice mismatch between Ge (5.66Å) and the fluoride film (5.60Å in calculation). The quality of the Ge film will be improved by optimizing the mixing ratio and the deposition conditions of the underlying fluoride film. The optimum conditions for the growth of $Ca_{1-x}Sr_xF_2$ and Ge are being investigated by X-ray diffraction analysis as well as RBS and TEM.

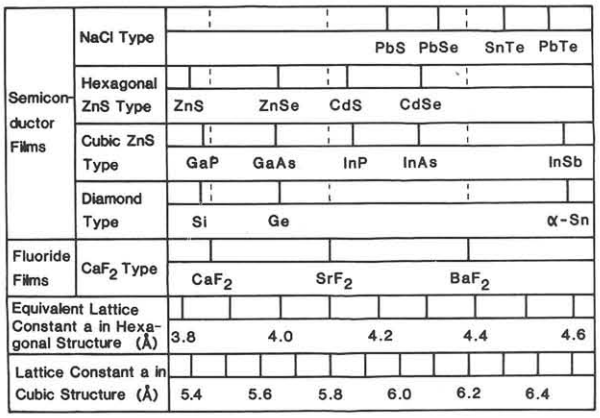

Fig.1

[References] (1) E.G.Chernevskaya et al; Soviet Phys. Solid State, 8 (1966) 169 (2) R.F.C. Farrow et al; J. Vac. Sci. Technol. 19 (1981) 415 (3) H.Ishiwara et al; Appl. Phys. Lett. 40 (1982) 66 (4) T.Asano et al; Proc. 13th Conf. Solid State Devices, Japan. J. Appl. Phys. Suppl. 20-1 (1982) 187 (5) B.Y.Tsaur et al; Appl. Phys. Lett. 38 (1981) 176

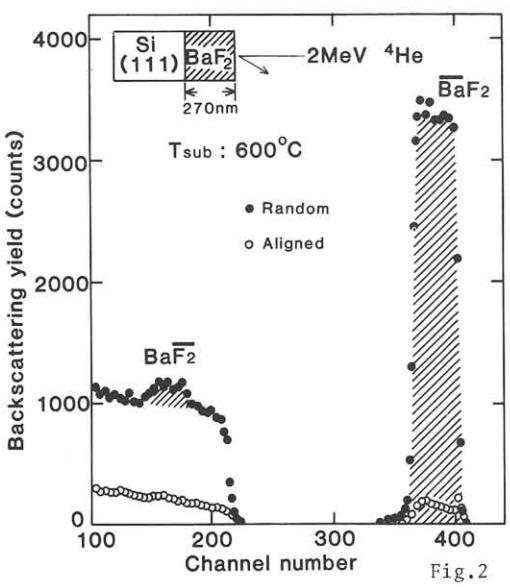

Fig.2

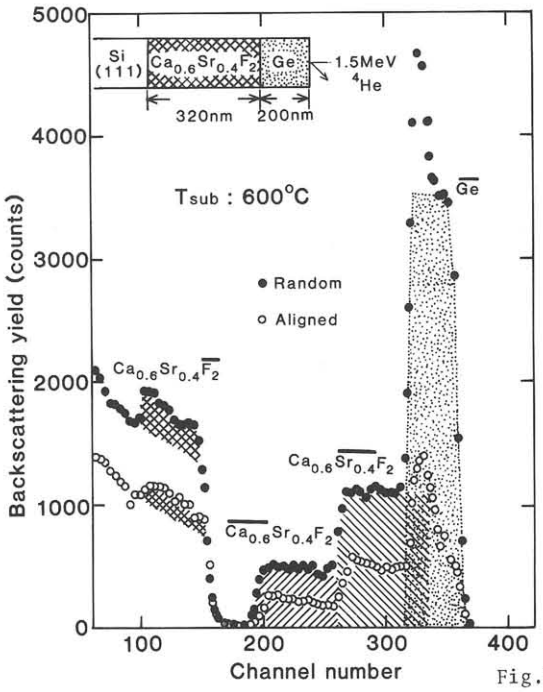

Fig.3