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13. ABSTRACT (Maximum 200 words) The epitaxial growth of $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2/\text{GaAs}(100)$ and $\text{GaAs}/\text{Ca}_x\text{Sr}_{1-x}\text{F}_2(100)$ is investigated. Optimum growth temperature of 530°C , growth rate of $1\text{ \AA}/\text{sec}$ and composition $x=0.47$ lead to very high crystallinity layers of mixed fluorides on GaAs. The growth of $\text{GaAs}/\text{Ca}_{0.47}\text{Sr}_{0.53}\text{F}_2(100)$, rendered much more difficult by the morphology and faceting of the insulating surface, is substantially improved by modifying the fluoride surface by electron irradiation prior to GaAs growth, and by a two-step growth sequence where the interface GaAs is grown at low temperature (300°C). Finally, the patterning of the fluoride layer is performed by e-beam exposure. Features as small as $1\ \mu\text{m}$ are drawn and developed on a 2000 \AA thick CaF_2 layer, opening the possibility of using the fluorides for wave-guides or re-growth of small III-V features.

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**Group II Cubic Fluorides as
Dielectrics for 3-D Integration and
GaAs-based Optoelectronics**

**Final Report
A. Kahn
August 1992**

U.S. Army Research Office
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A. Statement of Problem investigated

Under ARO contract number DAAL03-89-K-0035, we have investigated various aspects of the epitaxy and properties of mixed films of cubic fluorides grown on GaAs. The main goals of this research were: (1) to optimize the growth of mixed fluorides, i.e., $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2$, on GaAs and that of GaAs on mixed fluorides for 3-D integration; and (2) to investigate the sensitivity of the fluorides to electron-beam bombardment for patterning.

The interest in the fluorides for making crystalline insulators compatible with III-V compounds comes from various properties exhibited by these cubic compounds (CaF_2 , SrF_2 , BaF_2). First, they are wide band-gap low dielectric constant insulators (10-12 eV). Second, they crystallize in the fluoride structure and can be grown with good crystallinity on a number of substrates. Third, they are fully miscible and the lattice constant of mixed films can therefore be tuned almost continuously between that of Si and that of most III-V and II-VI compounds. In single crystal films, they can therefore be used as substrate for the re-growth of compound semiconductors, leading to the possibility of fabricating alternate semiconductor/insulator layers. Fourth, the evaporation of fluorides is entirely compatible with molecular beam epitaxy (MBE) environment and occurs through molecular sublimation which lead to stoichiometric films. Finally, fluorides decompose under electron bombardment (loss of F) and could be used for high resolution electron beam scattering.

Under a previous grant (DAAL03-86-K-0059), we initiated the study of $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2/\text{GaAs}$ grown by MBE. We investigated the growth as a function of substrate orientation and temperature. Under this latest grant, we focused on the optimization of the growth of $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2/\text{GaAs}$ and $\text{GaAs}/\text{Ca}_x\text{Sr}_{1-x}\text{F}_2/\text{GaAs}$ along the technologically important (100) orientation, as well as on the electron-beam patterning of fluoride thin

films.

B. Summary of important results

1. *Optimized growth of $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2/\text{GaAs}(100)$*

An extensive search of the optimum growth parameters for $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2$ on GaAs(100) was performed. Following the growth of 2000Å GaAs buffer layer, a 2000Å fluoride layer was grown at various rates and temperatures (T_G). The best layers were obtained for $T_G \simeq 530^\circ\text{C}$ at a rate of $\sim 1\text{Å}/\text{sec}$.

The crystallinity of the layers was studied via electron channeling and ion channeling (Rutherford backscattering, in collaboration with the Fort Monmouth Army laboratory). The best layers produced a minimum yield in ion channeling (χ_{\min}) of 4% at 2 MeV, which is very close to the theoretical limit and indicates an excellent crystallinity. These results constitute the state-of-the-art in fluoride epitaxy. The best fluoride layers were obtained for a relative concentration $x=0.47$ corresponding to lattice match to GaAs at a temperature of 300°C , intermediate between room and growth temperature. Cracks well aligned along the $\langle 110 \rangle$ direction, often observed in the fluoride films following cooling down, were tentatively attributed to boron contamination originating from a reaction between the pyrolytic boron nitride crucibles used for evaporation and the fluorides.

Finally, the (100) surfaces of the fluoride films were consistently found to exhibit (111) facets, in accordance with the need to lower the high electrostatic energy of the (100) surface.

2. *Growth of $\text{GaAs}/\text{Ca}_{0.47}\text{Sr}_{0.53}\text{F}_2/\text{GaAs}$*

Most of the effort supported by this grant was devoted to improving the epitaxy of GaAs on top of fluoride films. Typical structures involved a 2000\AA top GaAs layer grown on 2000\AA $\text{Ca}_{0.47}\text{Sr}_{0.53}\text{F}_2$ / GaAs buffer layer / GaAs(100).

The optimum growth temperature for the simple GaAs epitaxy was $\sim 600^\circ\text{C}$. These layers were found to exhibit a large density of anti-phase defects due to the faceted morphology of the (100) fluoride surfaces and leading to RBS χ_{min} superior to 30%. It was shown that GaAs nucleation on opposite (111) facets of small pyramids present on the (100) fluoride surface could and do lead to anti-phase growth.

In order to alleviate this problem, we investigated the growth of GaAs on fluoride surfaces irradiated with 2-5 keV electrons under As-flux. Electron-beam irradiation decomposes the top fluoride layers (with loss of F) and reduces the (111) faceting by eliminating the (100) electrostatic dipole. The freed Ca and Sr atoms also combine with As, instead of forming an oxide, and form a (Ca,As) or a (Sr,As) layer. This technique led to smoother (100) surfaces and a substantial improvement in the quality of the GaAs overlayers characterized by: 1. an improved surface atomic order (from RHEED); 2. an improved bulk crystallinity (RBS, $\chi_{\text{min}} = 24\%$); and 3. a lower density of anti-phase defects.

The quality of the GaAs growth was further improved through a two-step growth sequence. Following electron-beam irradiation of the fluoride, a thin GaAs layer was deposited at low temperature before raising the temperature to 600°C and growing the full 2000\AA layer. The low temperature buffer growth was designed to inhibit further reaction with the fluoride and reduce interface mixing. The thickness and growth temperature for this buffer layer were optimized at $\sim 200\text{\AA}$ and 300°C , respectively. This technique led to further improvements in the quality of the top GaAs surface morphology, surface atomic order, and bulk crystallinity. The best RBS χ_{min} , although still

insufficient for usable GaAs, was below 20%.

3. *Electron - beam patterning of fluoride films*

We have performed an in-depth investigation of electron - beam patterning of fluorides. Patterning results from a three step process: 1. electron - induced breaking of the CaF_2 and SrF_2 molecules (loss of F); 2. oxidation of Ca and Sr; and 3. dissolution of CaO and SrO in wafer (or acid). The elimination of F presumably results from an inter-atomic Auger transition which leaves F ions positively charged. These ions are expelled by electrostatic repulsion from the CaF_2 matrix.

Electron beam exposures were performed on 2000\AA fluoride layers with a PHI scanning electron microprobe ($\sim 150\ \mu\text{m}$ features) and a JEOL scanning electron microscope ($1\text{-}5\ \mu\text{m}$ features). We demonstrated complete removal of 2000\AA thick fluoride with electron doses of \sim few Coulombs/ cm^2 at electron energies 5-20 keV. The "development" of the electron - beam irradiated regions was investigated with Auger spectroscopy and X-ray dispersion analysis. The development step was considerably improved by introducing $\sim 5\%$ HCl in the water bath. Development times of a few minutes were obtained.

The excessive electron doses required for these patterning experiments are expected to be reduced by one to two orders of magnitude with the use of thin (few 100\AA) fluoride layers.

C. List of publications supported by this grant

1. $\text{Ca}_{0.55}\text{Sr}_{0.45}\text{F}_2$ / (100) GaAs by molecular beam epitaxy, S. Horng, A. Kahn, C. Wrenn and R. Pfeffer, Proceed. 2nd Int'l Conference on Electronics Materials, 1990 Materials Research Society, p. 229.
2. Growth of GaAs / $\text{Ca}_{0.45}\text{Sr}_{0.55}\text{F}_2$ / GaAs structures by molecular beam epitaxy, S. Horng, A. Kahn, C. Wrenn and R. Pfeffer, Materials Science and Engineering, *B9* (1991) 263.
3. Growth of GaAs/ $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{F}_2$ /(100)GaAs by molecular beam epitaxy, S. Horng, Y. Hirose, A. Kahn, C. Wrenn and R. Pfeffer, Mat. Res. Soc. Proc. *221* (1991) 175.
4. $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{F}_2$ / (100) GaAs for epitaxial regrowth and electron beam patterning, S. Horng, Y. Hirose, A. Kahn, C. Wrenn and R. Pfeffer, Proceed. Third International Conference on the Formation of Semiconductor Interfaces, Rome May 1991, Appl. Surf. Sci. *56-58* (1992) 855.
5. Electron beam patterning of epitaxial CaF_2 and $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{F}_2$ / (100) GaAs, Y. Hirose, S. Horng, A. Kahn, C. Wrenn and R. Pfeffer, J. Vac. Sci. Technol. *A10* (1992) 960.

D. Participating Scientific Personnel

1. Sheng-fu Horng, graduate student supported by the grant; completed his Ph.D. in June 1992; thesis sent separately to ARO.
2. Yutaka Hirose, graduate student supported by the grant;
3. The characterization of our films was performed in collaboration with Dr. R. Pfeffer and Mr. C. Wrenn from the Fort Monmouth Army Electronics Technology and Devices Laboratory.