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		Calcium Compounds	
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) The epitaxial growth of lattice matched $Ca_x Sr_{1-x} F_2 / GaAs$ and $GaAs / Ca_x Sr_{1-x} F_2$ heterojunctions by molecular beam epitaxy is investigated. These heterojunctions are potential candidates for realizing opto-electronic devices involving III-V Compound Semiconductors. The composition $x=0.5$ is chosen to minimize the lattice mismatch at room and growth temperatures. The fabrication of the layers involves the sequential growth of GaAs wafers of a GaAs buffer layer, a 2000-3000Å $Ca_{0.5} Sr_{0.5} F_3$ layer, and a top 500-3000Å GaAs layer. The growth along the (100), (111), (511) and (711) orientations is investigated. Optimum growth temperatures range from 500°C to 550°C for the fluorides, and			
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19. ABSTRACT

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550°C to 600°C for the GaAs. The orientation of the substrate is conserved throughout the three epitaxial layers. The bulk crystallinity, studied with ion scattering, is found to be excellent in the GaAs buffer layer, fair to good in the fluoride layer, and poor to fair in the top GaAs layer. The high Miller-index GaAs surfaces ((511), (711)) exhibit a regular stepped structure ((100) terraces) which contributes to the reduction of anti-phase disorder in the fluoride layer. It is also found that the (511) orientation is favorable for the growth of the top GaAs layer. Rough morphology and faceting at fluoride surfaces are identified as the main problems for the growth of high quality top GaAs layers. Post-growth thermal treatments and electron-beam exposure will be investigated as potential solutions. *Keywords: (511), (711), (100) terraces*

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Group II Cubic Fluorides as Dielectrics for III-V Compound Semiconductors

Final Report

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September 1989

U.S. Army Research Office

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A. Statement of problem investigated

Under ARO contract number DAAL03-86-K-0059, we have investigated the feasibility and optimum conditions for the epitaxial growth by molecular beam epitaxy (MBE) of semiconductor/insulator/semiconductor (SC/I/SC) systems of the type GaAs/Ca_xSr_{1-x}F₂/GaAs. These systems have recently received attention from several Japanese groups [1,2]. The interest in, and importance of, these systems for technological applications stems from the fact that mixed Ca_xSr_{1-x}F₂ are wide band gap insulators (10-12 eV) with the following properties: 1. they crystallize in the fluoride structure and can be grown with good crystallinity on a number of substrates; the fluoride film can therefore be used as a seed for the overgrowth of any crystal, in particular semiconductors; this extends therefore the possibilities for fabricating three dimensional SC/I/SC systems; 2. the lattice constant of the mixed fluoride can be adjusted to fit most semiconductors, in particular GaAs, by varying the relative concentrations of Ca and Sr; lattice matching between the insulator and the semiconductor can be exploited to realize interfaces with a low density of interface states; 3. the vapor pressures of CaF₂ or SrF₂ are very low, and their evaporation is compatible with standard MBE environment; 4. stoichiometric CaF₂ or SrF₂ films can be obtained by simple evaporation on non-dissociated molecules in vacuum; mixed films are obtained by co-evaporation of both species in controlled relative concentrations; 5. the large difference between the index of refraction of fluorides and GaAs makes these systems potential candidates for wave guiding and other optoelectronic applications; 6. fluorides decompose (loss of F) under electron bombardment and could possibly be used for high

resolution electron beam patterning.

B. Summary of important results

During the past three years, we accomplished a number of tasks described in the original proposal:

1. We designed and assembled an MBE chamber dedicated to the growth of GaAs and $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2$ films. The system consists of a UHV vacuum vessel pumped with a 400l/s ion pump; an evaporation flange with cryocooling and five temperature-controlled effusion cells for Ga, As, Si (dopant), CaF_2 and SrF_2 ; a reflection high energy electron diffraction (RHEED) optics; a temperature controlled sample holder for 1" wafers with flux monitor; a load-lock with transfer mechanism, degassing station and metallization port. The MBE chamber is coupled to a surface analysis system equipped with Auger electron spectroscopy (AES), low energy electron diffraction (LEED) and ion sputtering for depth profiling.
2. We established the growth conditions for GaAs/GaAs, an essential first step in the realization of the proposed SC/I/SC systems. We investigated the growth along four crystalline orientations, i.e. (100), (111), (511) and (711). The layers were analyzed with AES (composition), SIMS (contamination), RBS (bulk crystallinity), electron channeling pattern (surface orientation and near surface crystallinity), RHEED (surface structure during growth and growth rate), and SEM (surface morphology). We have obtained excellent growth along the (100) as well as the (511)-B orientations. RHEED

oscillations were routinely obtained for the (100) growth (not for the (511) growth because of the stepped structure of the corresponding surfaces), indicating good quality growth and very smooth morphology. The electronic quality of the layers were never good because of residual impurities (presumably F) in the GaAs layers (GaAs and fluorides are grown in the same chamber). The RBS measurements indicated good bulk crystallinity with x_{\min} of the order of 3-4% for the (100) and (511) layers (comparable to standard MBE work), and the surface structure measurements (RHEED, LEED, electron channeling pattern) showed the results expected from literature reports.

3. We established growth conditions for the fluoride layers on top of GaAs buffer layers and investigated the growth along the four orientations mentioned above. The best growth temperature was between 500°C and 550°C, and the growth rate 0.8 μm /hour. Fairly good bulk crystallinity was obtained for the (100), (111) and (511)-B orientations, with x_{\min} to 9.9%, 11% and 25%, respectively. These results are comparable or better than those reported so far by other groups for the *as-grown* layers (no post-growth thermal treatment) [3]. The fluoride (111) was found to be the most stable surface, in accordance with considerations of relative surface energy due to electrostatic dipoles. The (100) and (511) surfaces were found to exhibit (111) facets. The surface and near surface crystallinity of the fluoride layers were generally fair to good, with the best results obtained on the (100) and (511) films. Thermal treatments such as rapid thermal

annealing should improve the morphology and surface structure of these films. We also believe that the stepped structure of the high Miller-index GaAs surfaces should contribute to a reduction of anti-phase disorder in the fluoride layers.

4. Finally, we began the study of GaAs layers grown on top of $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2/\text{GaAs}(\text{buffer})/\text{GaAs}$. This is by far the most difficult part of the project, because of the overall degradation of crystallinity and morphology throughout the previous two layers. The work is, at present, only in its initial stage. The GaAs growth depends very sensitively on the structure and morphology of the fluoride surface and on eventual chemical reactions taking place at the interface. The crystalline quality of the films were generally poor to fair, with the best results obtained for the (511) orientation (RBS $x_{\text{min}} = 35\%$). We were able to verify that the orientation of the substrate is preserved, however, throughout the three epitaxial layers (GaAs buffer layer, fluoride layer, top GaAs layer). Future investigations will involve in-situ rapid thermal annealing of the fluoride films, which should improve their surface morphology, and electron beam irradiation of the fluoride which should improve the nucleation of the GaAs.

C. List of publications

1. "Photoemission study of the formation of interfaces between CaF_2 or SrF_2 and GaAs(110)," D. Mao, K. Young, R. Zanoni, J. McKinley, G. Margaritondo and A. Kahn, Phys. Rev. B**39**, 12735 (1989).

2. "Epitaxial growth of $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2$ on GaAs(100), (111), (511) and (711) surfaces," K. Young, J.M. Philips and A. Kahn, Proceed. MRS Meeting (April 1989) (in press).
3. "Study of (511) and (711) GaAs epi-layers prepared by MBE," K. Young, I.H. Campbell, J.M. Philips and A. Kahn, J. Cryst. Growth (to be published).
4. "GaAs/ $\text{Ca}_{.5}\text{Sr}_{.5}\text{F}_2$ /GaAs structures grown by MBE," K. Young, J.M. Philips and A. Kahn, J. Cryst. Growth (to be published).

Other manuscripts based on this work are in preparation and will be submitted during the next few months.

D. Participating scientific personnel

1. **Kwo-Hsiung Young**, graduate student supported by the grant; completed his Ph.D. degree in July 1989; thesis title "**Epitaxial growth of cubic fluorides on GaAs and GaAs on cubic fluorides by molecular beam epitaxy.**"
2. We collaborated with various scientists for the characterizations of our films:
 - Dr. J.M. Philips, AT&T Bell Laboratories (RBS)
 - Prof. P.M. Fauchet, Princeton University (Raman spectroscopy)
 - Dr. K. Jones and Dr. R. Pfeffer, Fort Monmouth Army Laboratory

E. References

- [1] H.C. Lee, H. Ishiwara, S. Kanemaru and S. Furukawa, Jpn. J. Appl. Phys. **26**, L1834 (1987).
- [2] H.C. Lee, T. Asano, H. Ishiwara and S. Furukawa, Jpn. J. Appl. Phys. **27**, 1616 (1988).
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