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MOLECULAR BEAM EPITAXY OF II-VI COMPOUND WAVEGUIDES

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Monocrystalline films of ZnSe and ZnTe have been grown by molecular beam epitaxy on GaAs(110) and (100) at 300 to 350°C. ZnTe(100) films are as smooth as the chemically-polished substrate (smooth to tens of Angstroms), while the others are considerably rougher. Films grown on BaF_2(100) are polycrystalline. ZnTe/Zn(SeTe)/GaAs(100) is proposed for an optical waveguide system.

14

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I. INTRODUCTION

II-VI compounds have considerable potential as electro-optic modulators in integrated optical circuits. The goal of our program has been to grow by molecular beam epitaxy (MBE) monocrystalline II-VI films of sufficient smoothness, purity, and crystallographic perfection to behave as low-loss waveguides.

The last report, submitted March 25, 1974, summarized work done since the start of the program, including substrate preparation, calibration and control of source material evaporation, film growth on CaF_2(111), CdS(0001A) and CdSe(0001A), and waveguiding measurements. The general findings were that at lower growth temperatures films were smooth but polycrystalline and at higher temperatures they were monocrystalline but rough. Waveguiding was demonstrated in ZnSe and ZnTe, but propagation losses were unacceptably high.

The present report discusses work performed since March 1, 1974, in which the effects of substrate orientation and structure on film growth morphology have been examined in an attempt to achieve smoother monocrystalline films. Growth of ZnSe and ZnTe on GaAs(110) and (100) were studied in particular detail.

II. RESULTS

A. SEM EXAMINATION

A sampling of films grown on (0001A) substrates was examined by a scanning electron microscope with the hope that the structural details of the film surfaces might give a clue as to the preferred growth plane, but the available 400Å resolution was insufficient for this purpose.

B. SUBSTRATE PREPARATION

Substrates employed included BaF_2(100), CdS(0001B), and GaAs(110) and (100). A chemical polishing procedure for BaF_2(100) which generates surfaces completely featureless under 400X Nomarski microscope examination had been developed in another program. Equally smooth surfaces were found under the present contract to be obtainable on CdS(0001B) using 4 parts of 2 1/2% sodium hypochlorite (liquid household bleach diluted 1:1 with water) to 1 part precipitated silica. Procedures were similar to those reported for CdS(0001A).[1] GaAs was polished with Mirrolite (Materials Development Corp.), but better results were obtained by using 90% of the recommended concentration. While resulting surfaces were mirror-smooth to the eye, they had a slight texture under Nomarski examination (perhaps tens of Angstroms).

BaF_2(100) substrates produced good LEED (low-energy electron diffraction) patterns after 600°C, 1 minute heat-cleaning at 10^{-9} Torr. CdS(0001B) substrates gave patterns indicating considerable disorder and faceting after either heat-cleaning or ion-bombardment under various conditions. Since no appreciable contamination was detectable by Auger spectroscopy, it was concluded that CdS(0001B) must be a thermodynamically unstable surface and therefore unsuitable for epitaxy. GaAs heat-cleaned at 600°C gave LEED patterns which were well-ordered but which also had high diffuse background due to the residual surface carbon which is typical of lower-bandgap semiconductors and of metal surfaces. The background was somewhat reduced by ion bombardment, but this procedure did not noticeably improve epitaxy, and the carbon was always readily buried by the growing film. Therefore, GaAs was generally only heat-cleaned.

C. ZnSe GROWTH

We had heretofore grown II-VI compounds by evaporating the elements rather than the compounds because these were obtainable in higher purity and because we wished to examine the effect of II/VI evaporation rate ratio on film growth. Selenium, however, is a difficult element to handle under vacuum, having a vapor pressure of 10^{-4} Torr at only 165°C, and in addition existing as a multitude of polyatomic molecules[3] which influence sticking coefficient and flux monitoring. ZnSe was therefore grown here from 5-nines Eagle-Picher ZnSe crystallites. Deposition rate was calculated from the reported $(\mathrm{ZnSe})_s \rightleftharpoons \mathrm{Zn}_g + 1/2(\mathrm{Se}_2)_g$ equilibrium constant,[4] using the Knudsen effusion equation and system geometry as discussed previously,[5] and is plotted in Figure 1. Actual growth rate was about 1/5 of that calculated; this fraction is plotted as "sticking coefficient" in Figure 2a. Moreover, the Se/Zn flux ratio measured by the mass spectrometer here was about 1/5 of that measured previously in growth from the elements when Se/Zn had been "balanced" by the quartz crystal technique[5]. These observations suggest that the sticking coefficient of Se is about 1/5 at the ZnSe growth temperature, and that the "balanced" Se/Zn ratio in growth from the elements actually amounted to a X5 excess of impinging Se.

General trends in crystallographic and topographic quality of ZnSe films grown on GaAs(110) and (100) are plotted as functions of growth temperature in Figure 2a, "1" representing very sharp LEED patterns with zero diffuse background and completely featureless surfaces under 400X Nomarski examination, "0" representing no LEED patterns and surfaces rough to the eye. From 300 to 350°C, films grew epitaxially and LEED patterns were very good on both (110) and (100). These patterns were always better than those from the substrate, and in two cases where no pattern was observable from the (100) substrate, good (100) LEED patterns were still obtained from the films. Under the same conditions, ZnSe grew polycrystalline on a BaF_2(100) substrate.

All ZnSe films on GaAs(110) and all films thicker than 1/4 micron on GaAs(100) were rougher than the substrate, becoming worse with increasing substrate temperature as indicated on Figure 2a. Roughness increased with thickness, and films thicker than 1 micron were rough to the eye. For similar conditions, films were rougher on (110) than (100).

The results of Figure 2a were the same at both 1/3 and 3 microns/hour growth rate.

D. ZnTe GROWTH

ZnTe was grown from the elements, as previously,[5] at 2 microns/hour. Figure 2b shows sticking coefficient, crystallography and topography as Figure 2a did for ZnSe. Sticking coefficient was unity up to 350°C, and high quality epitaxy was obtained from 300 to 350°C on both GaAs(110) and (100). It should be noted that under the same conditions, ZnTe had grown polycrystalline on both BaF_2(100) and CaF_2(100) in October, 1973 (not reported previously). These results are consistent with those for ZnSe on BaF_2(100), above. 1 micron-thick films on GaAs(100) were as smooth as the substrate, and on (110) were somewhat rougher, though still smooth to the eye.

A series of two-layer films, ZnTe on ZnSe, were grown on GaAs(110) and (100) as potential waveguide systems, the ZnSe acting as a low-index (n=2.6) buffer layer between the ZnTe guide (n=3.0) and the high-index GaAs (n=3.6). ZnTe on a 1/10 micron ZnSe(100) film was as smooth as the substrate, but the buffer layer was too thin to allow propagation of 6328Å light. ZnTe on 1/10 micron of ZnSe(110) and on 3/4 micron of ZnSe(110) and (100) was rough to the eye and could not be coupled into.

III. CONCLUSIONS

Substrate orientation and structure appear to be key factors in II-VI compound growth. While epitaxy of ZnSe and ZnTe has been obtained in this laboratory on all three basic cubic planes, the required conditions and the film topography vary considerably from plane to plane. On (100), epitaxy has been obtained for GaAs but not for BaF_2 or CaF_2 substrates. By comparison, Holt[6] obtained epitaxial ZnTe by vacuum evaporation on CaF_2(111) and BaF_2(111) but not on NaCl (100). Epitaxy of ZnSe by vacuum evaporation on GaAs(100) has been reported by other workers[7], but only above 350°C, possibly because of their less hard vacuum conditions (10^{-6} vs. 10^{-9} Torr). Film smoothness is a strong function of substrate plane; in order of decreasing smoothness, (100) > (110) >> (111). The temperature range for epitaxy is also much narrower on (111) than on the other planes. A similar trend has been found for ZnSe vacuum evaporation on Ge[8], where the temperature range of epitaxy decreased as follows: (100) > (110) > (111), (111) giving no epitaxy.

In summary, (100) is clearly the preferred plane for ZnSe and ZnTe epitaxy by vacuum evaporation, but for zincblende and not for fluorite or rocksalt-structure substrates. Since zincblende crystals are noncentrosymmetric and since the consequent internal field components are stronger parallel to (100) planes than to (110) or (111), perhaps it is the presence of these parallel field components which is the critical factor in encouraging epitaxy. Strangely, the situation for liquid phase epitaxy of ZnTe on ZnSe is the opposite: (111) films are much smoother than (110) or (100) films.[9]

For further MBE work directed at waveguide modulators, a system based on ZnTe rather than on ZnSe is preferable for several reasons: far smoother monocrystalline ZnTe films can be grown, Se is difficult to handle in MBE, and ZnTe has twice the electrooptic coefficient of ZnSe. The substrate should be InAs(100), whose lattice constant matches ZnTe much more closely than does that of GaAs. The second layer of the required two-layer film would be $ZnSe_xTe_{1-x}$ or $Zn_{1-x}Cd_xTe$, where $x \to 0$.

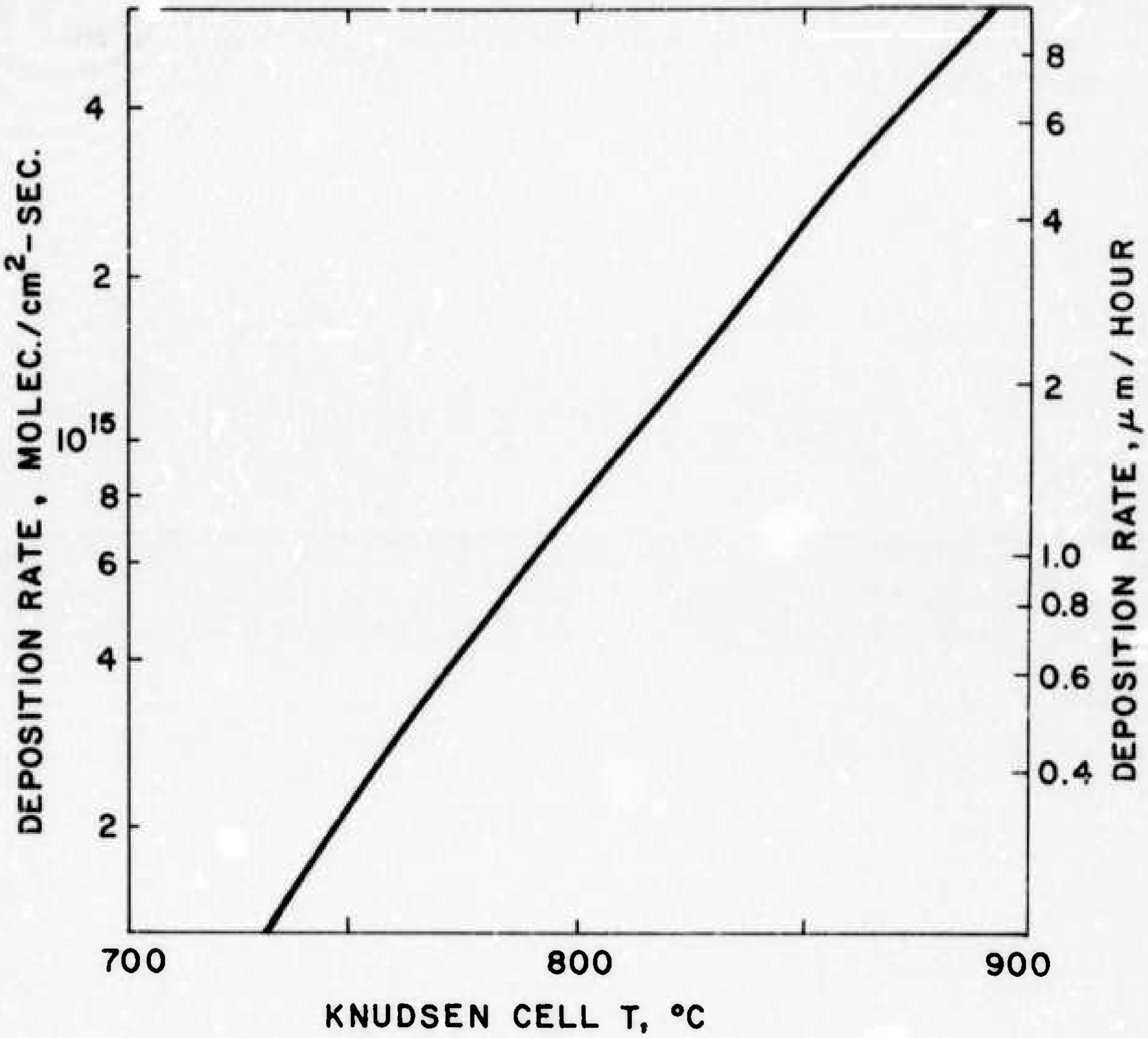
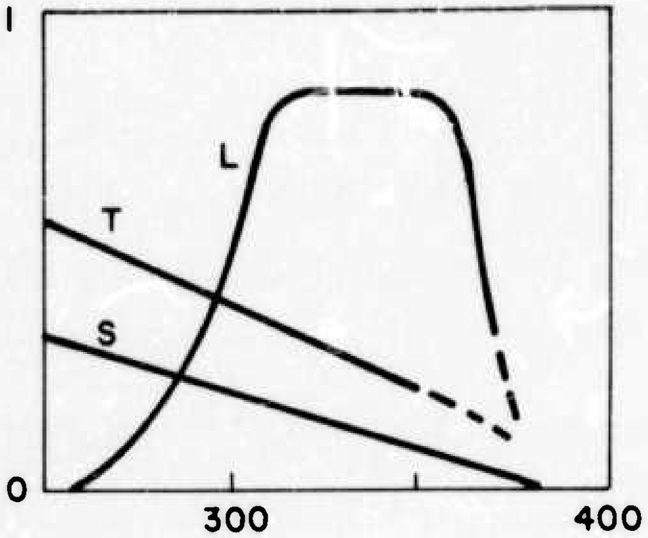
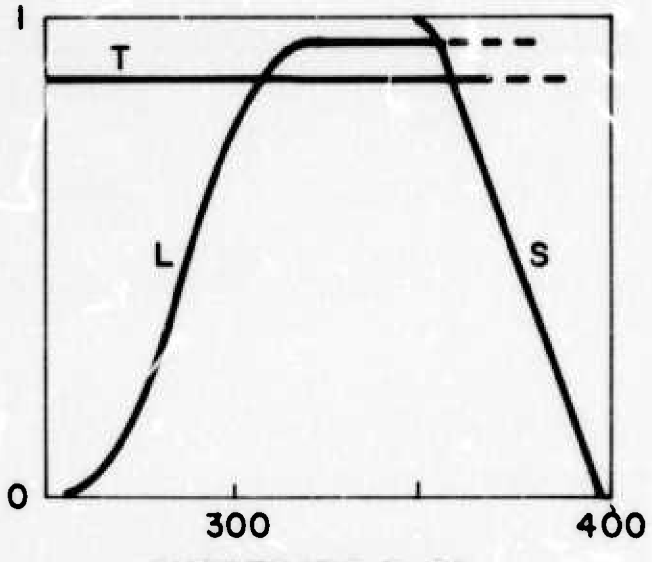


FIG. I ZnSe EVAPORATION

(3mm dia. orifice, 5 cm substrate distance)



a. ZnSe



b. Zn Te

FIG. 2 GROWTH CHARACTERISTICS ON GaAs
(L = LEED Pattern quality, T = Topographic quality, S = Sticking coefficient)

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