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Characterization of $Be_xZn_{1-x}O$ Thin Films Grown by Pulsed Laser Deposition

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Introduction

The development of electronics for high-power applications and for use in extreme conditions, e.g., at high temperatures or under heavy radiation loads, have shown the limits of traditional semiconductors like Si. The large band gap, good thermal conductivity and good stability at high temperature are the main advantages of wide-gap semiconductors in helping to overcome the limits of silicon. In optoelectronics, wide-gap semiconductors are used in UV light emitters and sensors. Generally, wide-gap materials are excellent insulators due to the low intrinsic carrier density but semiconducting behavior is in some cases possible by adding dopants. In this study, the focus is on the BeO-ZnO material system.

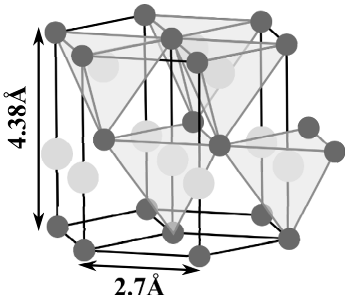

Figure 1: Structure of wurtzite BeO. Oxygen atoms are shown in dark gray, Be in light gray.

The cell parameters of wurtzite BeO are $a = 2.70$Å and $c = 4.38$Å (Fig 1). Beryllia has a large band gap, $E_g = 10.6$ eV, a high Debye temperature, $\theta_D = 1270$ K, a high melting point of 2507°C, and a high resistivity of 10^{13} Ωcm. The low atomic mass of Be is an advantage for applications where high-energy particles or high radiation loads are present, for example, in nuclear and aerospace industries.

The characteristics of semiconductors are commonly tuned by adding dopants to a parent compound. In this research, beryllia was alloyed with zinc oxide. ZnO is isostructural with BeO but has a lower band gap ($E_g = 3.3$ eV). The cell parameters and the band gap of $Be_xZn_{1-x}O$ have been reported to be controlled by the Be content, x.[1]

Experimental

The BeZnO alloy thin films were grown by pulsed laser deposition (PLD). The deposition system was composed of a vacuum chamber, an O_2/N_2O gas supply, a diode laser for substrate heating, and a high brilliance, high frequency, low fluence KrF excimer laser (200 Hz, 12 mJ, 248 nm). The growth of BeO and $Be_xZn_{1-x}O$ thin films on Al_2O_3 (001) and Nb:$SrTiO_3$ (111) are discussed in the present work. The ablation plume was characterized using a time of flight measurement. The film crystallinity was investigated by X-ray diffraction measurement and the Be content, x, of the $Be_xZn_{1-x}O$ films was estimated from the symmetrical $2\theta/\theta$ scans. The band gap energy shift of the alloy films was measured by optical transmission and reflectivity spectroscopy. The photocarrier behavior was investigated by looking at the conductivity response of the films to a chopped monochromatic light beam. A high-temperature probe was used for dosimetric thermally stimulated electron emission measurements.(TSEE)

Results & Discussion

BeO films

A crystalline BeO thin film was successfully grown, demonstrating the possibility to deposit very wide gap materials with a pulsed laser technique. The phase formation of BeO films on sapphire(001) was investigated for different background pressure and substrate temperature combinations. Three growth regimes were identified: amorphous growth, crystalline growth, and rapid sublimation.(Fig 2) The optimum conditions for crystalline beryllia growth were identified for an oxygen pressure of 1 mTorr and a 500°C substrate temperature. A noteworthy strained crystalline phase was obtained in a room-temperature growth process at low background oxygen pressure.

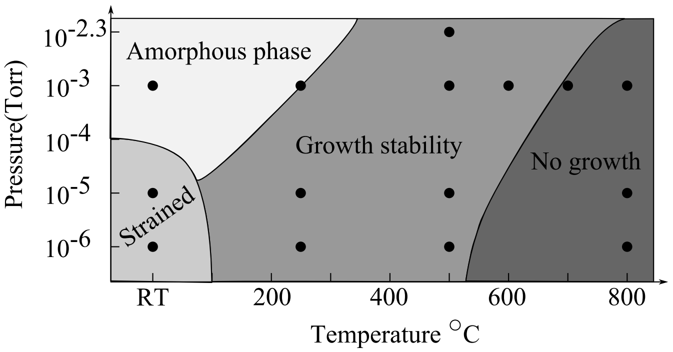

Figure 2: Growth regime diagram for BeO thin films grown on sapphire (001).

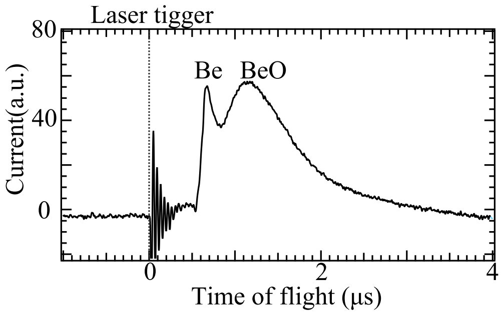

Figure 3: Time-of-flight histogram of ion current in a BeO ablation plume.

The absence of film growth at temperatures above 600°C was investigated by analyzing the species ablated from the target. The deposition plume composition was measured to obtain additional information on the film growth kinetics. The ablation plume composition showed the presence of at least two charged species.(Fig. 3) One of the species was identified as beryllium, suggesting that the re-sublimation of the deposited species may be responsible for the rapid loss of growth rate at elevated temperatures.

The polarity of crystalline BeO films was measured by pyroelectric analysis of thin beryllia films deposited on metallic Nb:$SrTiO_3$ (111) substrates. A capacitance-voltage profile was used for determining the relative permittivity of BeO thin films.

$Be_xZn_{1-x}O$ films

A crystalline phase was obtained over a substantial range of $Be_xZn_{1-x}O$ film compositions. The determination of the Be content by X-ray diffraction was compared with the expected Be-content. Based on the symmetrical $\theta/2\theta$ scans, the evolution of the crystallinity was investigated as a function of Be-content.(Fig. 4) An instability of the crystal structure was observed as the Be content approached 50%. A model was suggested to explain the structural change due to the incorporation of beryllium atoms in the ZnO lattice. The transmission and reflectivity measurements confirmed the possibility of band gap energy engineering. The quadratic relation between the $Be_xZn_{1-x}O$ film band gap energy and the Be content x showed a strong curvature due to a substantial difference between beryllium and zinc ionic radii.

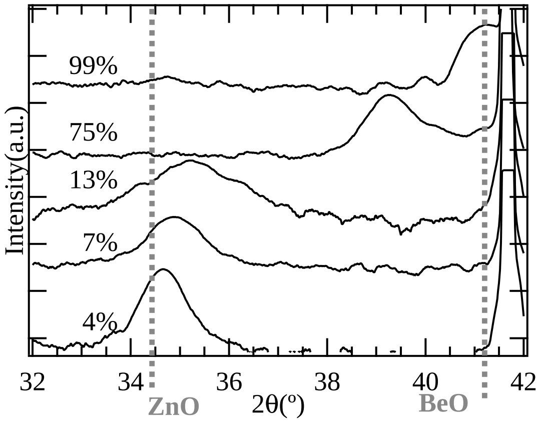

Figure 4: XRD patterns of $Be_xZn_{1-x}O$ films. The positions of the BeO(002) and ZnO(002) peaks are shown. The percentage numbers indicate the Be content.

The wavelength-dependent photoyield was measured for the BeZnO films. Strong wavelength-dependent peaking of the photocurrent in comparison with the dark current was seen for films with a high Be content. The edge of the photoyield peaks was used to derived the energy of the band gap. The values were compared with reference data found in the literature and the data obtained by optical spectroscopy. The photocurrent response times of the BeZnO films were found to be on the order of 10 ms or 100 ms and did not show strong variation with the Be content. The defect structure shows a distribution of defects between the Fermi level and the conduction band and was attributed to shallow donors close to the conduction band.

It was demonstrated that BeZnO films can be used as a dosimeter, similarly to BeO thin films. A 4% doped ZnO thin film was irradiated by an X-ray source, resulting in the trapping of electrons in the deep levels in the band gap. Thermally stimulated electron emission(TSEE) was observed by performing a current measurement during high temperature annealing. (Fig. 5)

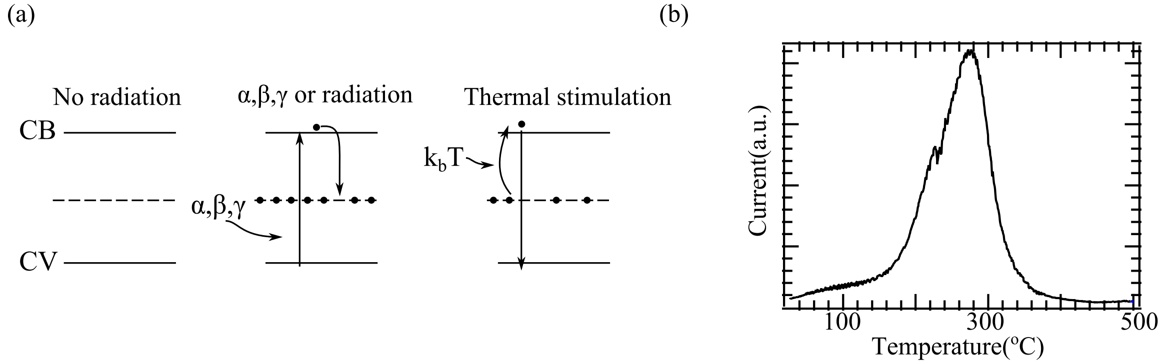

Figure 5: (a) Schematic of the electron trapping and TSEE. (b)The observed sample current under an applied bias of 15 V during a heating cycle after x-ray exposure.

Conclusions

The possibility of depositing BeO, a wide band gap insulator with $E_{\mathrm{g}} = 10.6$ eV, was demonstrated using Pulsed Laser Deposition. A temperature pressure growth phase diagram was drawn for BeO films grown on sapphire. Further investigations on the ablation plume was carried out by time-of-flight measurement.

The alloying of BeO and ZnO was demonstrated over a substantial range of the composition space. The relation between the expected Be content and the Be content determined by X-ray diffraction was discussed in relation to the crystal quality and the film morphology. The possibility of band gap engineering was demonstrated for $\mathrm{Be}_x\mathrm{Zn}_{1-x}\mathrm{O}$ alloy films.

In order to evaluate the prospects of using beryllia-based films in radiation detector applications, the photoyield of $\mathrm{Be}_x\mathrm{Zn}_{1-x}\mathrm{O}$ was investigated. The alloy film response times were measured and attributed to the presence of shallow donors close to the conduction band edge.

References

[1] Y.R. Ryu, T.S. Lee Lee, and al. Wide-band gap oxide alloy: BeZnO. *Applied Physics Letters*, 88(5):052103, 2006.

Presentation

- JSAP 2012 Autumn meeting: BeO thin film growth on Sapphire
- JSAP 2013 Spring meeting: Fabrication of BeO-ZnO alloy phase thin films

Future plans

- Investigation of the Be content by XPS measurement
- Determination of the linearity of the thermocurrent dosimeter
- Exploration of the doping of BeO by Copper or Scandium