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研究課題名（和文）軽元素の半導体

研究課題名（英文）Light-element semiconductors

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研究成果の概要（和文）：パルスレーザー堆積手法によってベリリウム酸化物(BeO)、そして亜鉛をドープしたベリリウム酸化物(Be-Zn-O)の薄膜結晶を作製した。BeO 結晶の薄膜が安定して成長する作製条件を探索した。その結果、BeO 薄膜が室温でも成長することが新しくわかった。また、Be-Zn-O の薄膜結晶の実験では、Zn または Be が過剰な組成領域でのみ混晶結晶が成長することが見出された。このような Be-Zn-O 混晶の薄膜結晶を用いて X 線線量の測定を行うことも可能となった。

研究成果の概要（英文）：The growth of BeO and BeZnO thin films by pulsed laser deposition was studied. A stability diagram was constructed for the growth of crystalline BeO films. It was discovered that it is possible to grow crystalline films even at room temperature. The available alloying limits were determined for both Zn- and Be-rich BeZnO semiconductor films. X-ray dosimetry function was evaluated in Be-doped ZnO films.

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１．研究開始当初の背景

Development of new semiconductor materials is the key to expanding the use of electronic devices in severe environmental conditions, such as high temperatures or heavy ionizing radiation loads. Practical applications include high-temperature / high-pressure sensors and electronics in deep-bore drilling for oil and gas, industrial process control applications in high-temperature materials processing, various monitoring and recovery applications in the nuclear industry, radiation-resistant electronics for the aerospace industry, and sensors for high-energy physics experiments. Due to this, various nitride and carbide semiconductor materials have recently been developed. The question, which wide-gap semiconductor material has the lowest average atomic mass and hence the lowest radiation sensitivity, remains open.

２．研究の目的

The purpose of this project was to explore the possibility of developing beryllia-based electronic materials. Beryllium oxide itself is a very wide gap insulator. Various alloy phases, however, are theoretically possible and have been studied to some extent. In this project, the aim was to explore the possibility of growing beryllia based alloy phases, specifically $Be_xZn_{1-x}O$, in thin film form by pulsed laser deposition (PLD), possibly leading to the development of novel radiation-hard device structures for sensors and basic switching applications.

３．研究の方法

The focus of this study was on developing growth techniques for fabricating pure beryllia and beryllia-based thin films by pulsed laser deposition. The films would then be characterized in terms of structure, conductivity, photoconductivity and morphology in order to study the possibility of using BeO-ZnO and other alloys in practical electronic applications. The films would then be tested for possible use in radiation sensing devices. The planned work was thus divided into four stages:

(1) The development of a pulsed laser deposition (PLD) system for depositing very wide gap materials, such as BeO. Since the BeO bandgap is 10.6 eV, whereas the KrF excimer laser photon energy is only 5 eV, it is difficult to evaporate pure BeO in normal PLD chambers. A special deposition chamber and a unique low-energy, high repetition rate excimer laser was set up for this project.

(2) BeO has the wurtzite crystal structure, similar to ZnO, except that the lattice parameter of BeO is much smaller. It was therefore questionable how easy it would be to stabilize the growth of epitaxial BeO or BeZnO films on commonly available substrates, such as sapphire or $SrTiO_3$(111).

(3) Alloy phases containing Be were studied in order to evaluate the electronic properties of the alloy films. The main focus was on determining the solubility limits of Be in ZnO and Zn in BeO. The films were characterized mainly by structural, transport, and photoconductivity measurements.

(4) The final planned task was to demonstrate radiation sensor device functionality in an alloy material. A high-temperature transport measurement was constructed for this part of the project.

４．研究成果

The project results are listed according to the original proposed subtasks.

(1) A micro pulsed laser deposition chamber (Fig. 1) was adapted for the growth of BeO films by constructing a suitable heating system and a special double-target holder for evaporating sequentially BeO and ZnO targets. This setup allowed the alloying ratio of BeO and ZnO to be chosen freely for alloy material growth. A time-of-flight ion spectroscopy setup was added to the thin film growth chamber to study the composition of the laser ablation plume during target material evaporation. This was necessary in order to determine the role of be metal oxidation kinetics on the crystalline phase formation.

Fig. 1 Pulsed laser deposition system adapted for very wide-gap material deposition.

(2) The growth of BeO films on sapphire substrates was studied in detail. A growth mode stability diagram was constructed for the formation of crystalline or amorphous BeO films grown on sapphire substrates in order to determine a practical process parameter window. For a light element such as Be, the risk of cation loss by resputtering from the surface of a film by the high-energy ionic species in the ablation plume is high. It was thus necessary to determine the stability of BeO growth before alloy phases could be studied. The stability diagram shows several different types of growth as a function of

substrate temperature and the ambient oxygen pressure (Fig. 2). Better crystallinity can be obtained at higher temperature, but this is only possible at higher effective oxygen pressures. It is likely that better-quality BeO films could be grown with ozone or other oxygen radical gas sources.

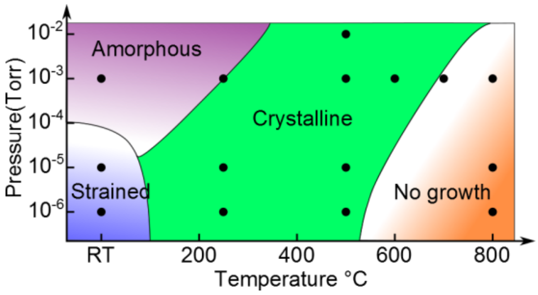

Fig. 2 BeO crystal growth stability diagram.

X-ray diffraction analysis showed that crystalline BeO films can be grown even at room temperature. Optimum film growth occurred at 500 to 600°C. At higher temperatures, Be metal loss from the surface prevented film growth. It was thus understood that the film growth stability is determined by the oxidation kinetics of Be metal on the film surface.

Surface morphology and x-ray diffraction analysis of the films showed that the crystallinity is limited by grain formation, which is driven by the lattice mismatch between the BeO film and the sapphire substrate. A 30 degree in-plane lattice rotation was observed for the BeO films on sapphire. In order to fabricate device structures for electrical measurements, BeO films were also successfully grown on hexagonal surfaces of metallic Nb:$SrTiO_3$(111) substrates.

(3) Theoretical predictions have suggested that there may be stable alloys in the $Be_xZn_{1-x}O$ phase diagram. Optimization of alloy film growth showed that in practice, alloying is possible only close to either end composition (Fig. 3). Deviations from the usual Vegard's law occur for intermediate compositions, indicating the presence of a large number of interstitial defects in the crystal when the composition is close to $Be_{0.5}Zn_{0.5}O$.

The alloy films were analyzed by measuring optical absorption spectra and photoconductivity lifetimes under chopped light illumination at various wavelengths. A systematic band gap shift was observed with increasing Be content in the films. Concomitant with the loss of a sharp x-ray diffraction peak for Be doping levels of 20% or more, a sharp optical absorption edge developed several absorption steps and showed strong broadening. This result is consistent with the appearance of structural or phase inhomogeneity in the films.

Time-dependent photoconductivity

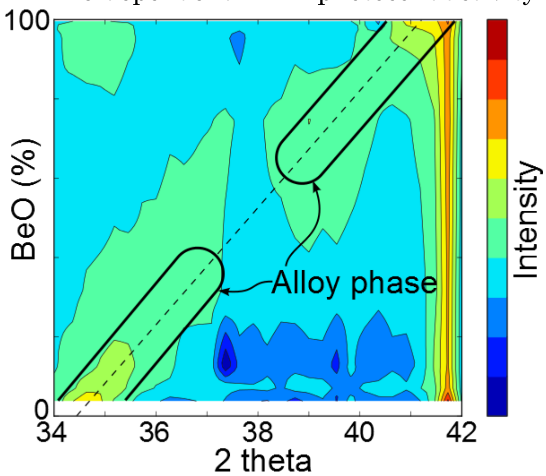

Fig. 3 $Be_xZn_{1-x}O$ alloy phase formation stability regions for $x<0.2$ and $x>0.8$.

measurements showed the presence of several relaxation phenomena. Two main relaxation time constants were determined, in the range of 100 ms and <10 ms. The appearance of long time constants indicates the presence of relatively deep in-gap defect states in the alloy films. The photoconductivity was measured over macroscopic distances between wire-bonded aluminum electrodes. It may be possible to obtain much faster response times in measurements that utilize depletion layers in BeZnO Schottky junction devices.

(4) The BeZnO alloy family has been mostly suggested as a potential ultraviolet (UV) photodetector material for solar-blind aerospace applications. The possibility of using a ZnO alloy phase for detection of higher-energy photons or high-energy particles had not been studied so far. The presence of deep trap states in the BeZnO films, as suggested by the photoconductivity measurements, indicated that it may be possible to use the material in a dosimeter device. This functionality was tested by exposing alloy

film samples to a laboratory x-ray source (Cu Ka) and measuring the current generated upon heating of an exposed film (Fig. 4). A special high-temperature transport measurement setup was constructed for these measurements, allowing sample currents to be measured at temperatures of up to about 750°C.

As a result of thermal detrapping, a large current was observable during the initial heating of a radiation-exposed $Be_xZn_{1-x}O$ film even for a very low Be doping level of 4%. Further work will be necessary to determine the quantitative charge generation rates for various incident photon energies.

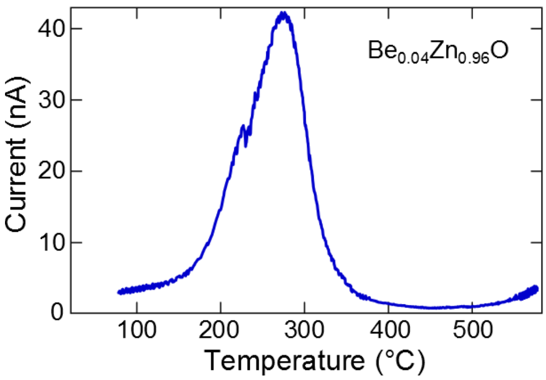

Fig. 4. Thermal detrapping current during the initial heating of a $Be_{0.04}Zn_{0.96}O$ film after x-ray exposure.

５．主な発表論文等

〔学会発表〕（計３件）

1. “BeO-ZnO alloy thin films”, P. Thomas, R. Takahashi, and M. Lippmaa, 2013 JSAP-MRS Joint Symposia, Sep. 16-20, 2013, Kyoto

2. “BeO-ZnO 混晶薄膜の作製”, T. Peltier, 高橋竜太、Mikk Lippmaa, 第 60 回応用物理学学術講演会　神奈川工科大学　2013 年春期　3/27-3/30

3. “サファイア基盤上における BeO 薄膜の作製” T. Peltier, 高橋竜太、Mikk Lippmaa, 第 73 回応用物理学学術講演会　愛媛大学　2012 年秋期　9/11-9-14

〔その他〕
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６．研究組織

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