Microstructural Analysis of Optical Materials

Introduction

"Photonic applications using the II-Vi semiconductor Zinc Oxide (ZnO) are becoming increasingly prevalent, and research into even more uses is exploding, with hundreds of labs looking into the material's unique properties" [1]. One reason for increased interest in ZnO as a potential replacement to gallium nitride and other semiconductors is because it is environmentally benign. In fact, ZnO is biologically compatible which makes it especially well suited for potential medical applications. ZnO is transparent at wavelengths in the visible part of the electromagnetic spectrum and opaque at ultraviolet wavelengths. It also exhibits piezoelectric and pyroelectric behavior. ZnO has been produced in a wide variety of forms tailored for specific optoelectronic applications. A new form produced by a vapor growth process has been characterized using electron backscatter diffraction (EBSD) in the scanning electron microscope (SEM).

Single crystals of materials like Magnesium Fluoride (MgF_2), Alumina (Al_2O_3) and Magnesium Aluminate ($MgAl_2O_4$) are capable of transmitting both infrared (IR) and visible light (see Figure 1). With recent technological advances in the formation of nanostructured materials, it is now possible to fabricate these materials in polycrystalline form and still retain their transmittance properties. The fabrication of polycrystalline ceramic materials reduces the cost significantly in comparison to the fabrication of single crystal materials. These polycrystalline ceramics can be fabricated in highly dense compacts which mitigates pore formation. Pores are deleterious to light transmission. As these are ceramic materials, they have high strength and hardness and, therefore, good damage and thermal-shock resistance. Thus, these materials are well suited for application as protective domes and windows. In order to produce materials with good IR transmission it is important to understand those factors which affect the light-scattering properties of polycrystalline materials. One of these factors is grain size (or more precisely grain boundaries). Studies [2, 3] have shown that decreasing the grain size actually improves the transparency in MgF_2 and Alumina. Another factor that affects the transmittance is the preferred crystallographic orientation of the constituent crystals or texture [4]. EBSD is an ideal tool for characterizing such microstructural characteristics. In addition, the chemical composition of these materials affects their performance. Energy Dispersive Spectroscopy (EDS) is well suited to not only measuring the chemical composition but also its spatial distribution within the microstructure. Examples of EBSD and EDS analysis of these materials are described in the following sections.

Figure 1. Two polycrystalline $MgAl_2O_4$ samples showing varying levels of transparency.

Zinc Oxide [5]

Figure 2 shows well-faceted ZnO microfibers with periodic junctions. The microfibers were prepared by an evaporation and deposition process. Fibers can be produced with spacings between the junctions ranging from 5 mm to 30 mm. The spacing can be controlled by controlling the growth conditions. Several techniques were employed to characterize these materials including X-ray diffraction (XRD), energy-dispersive X-ray (EDX) analysis, scanning electron microscopy (SEM), electron backscatter diffraction (EBSD) and photoluminescence (PL) microscopy. In particular, EBSD was used to characterize the anisotropic growth mechanism of the fibers.

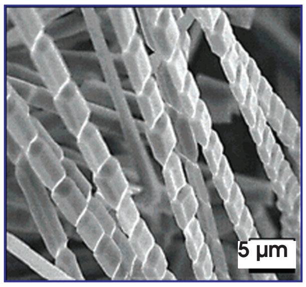

Figure 2. ZnO microfibers with periodic junctions with 6.2 µm spacing.

An anisotropic microfiber growth model was postulated as shown in Figure 3. This was confirmed by EBSD measurements on several fibers. An example is shown in Figure 4. A small series of orientation measurements were made using EBSD made along the length of the fiber. From analysis of the individual orientation measurements it was first found that the fibers were indeed single crystals.

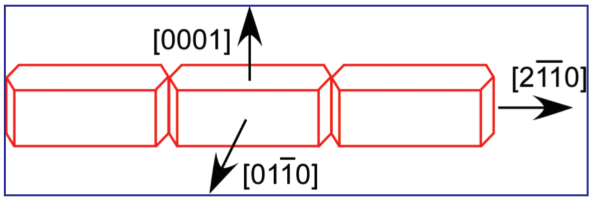

Figure 3. Microfiber anisotropic growth model.

Through pole figure analysis of the data, it was confirmed that the growth direction of the fibers is $\langle 2\bar{1}\bar{1}0 \rangle$, the "side" surfaces are {0001} planes and the top and bottom surfaces are $\{01\bar{1}0\}$ planes. The base of the fiber is formed by fast growth along the $\langle 2\bar{1}\bar{1}0 \rangle$ direction followed by slow growth along c-axis [0001] forming the regular prisms.

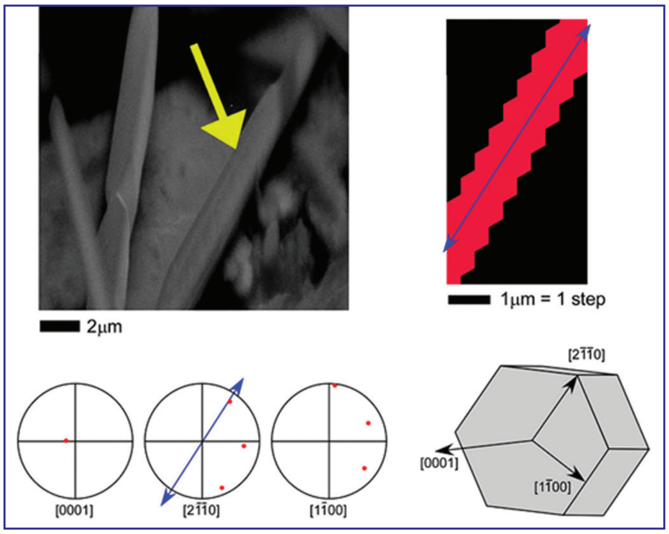

Figure 4. EBSD measurements and pole figure analysis.

Photoluminescence studies showed that the optical character of the fibers was related to the structure, as can be observed in Figure 5. The photoluminescence behavior means that these modulated fibers could serve as microscale waveguides and make possible the creation of microscale light-emitting arrays as well as bar codes used in biotechnology and electronics. EBSD has been used to characterize ZnO in other forms and applications. For example on polycrystalline ZnO varistors [6] and powder compact specimens [7] single crystal nanoscrews [8] and tetrapods where each leg of the tetrapod is a single crystal [9].

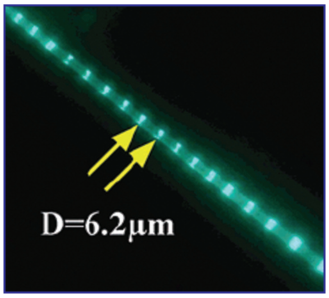

Figure 5. Photoluminescence micrograph for the type of fibers shown in Figure 2.

Magnesium Fluoride

Magnesium Fluoride (MgF_2) has a tetragonal crystal structure. Wen and Shetty [2] have shown that the grain size affects optical transmittance in polycrystalline MgF_2. Figure 6 shows orientation maps of MgF_2 in the as hot pressed form and then annealed at different annealing temperatures. The orientation data was obtained using EBSD. Such maps are often termed OIM™ (Orientation Imaging Microscopy) maps. EBSD is especially well suited to characterizing grain size in these materials. The ability of these materials to transmit light makes it difficult to get accurate grain size measurements using conventional light microscopy. In addition, light microscopy does not have the spatial resolution to resolve the microstructure at the smaller grains sizes. It is clear from the OIM™ maps shown here that the higher annealing temperatures promote increased grain growth.

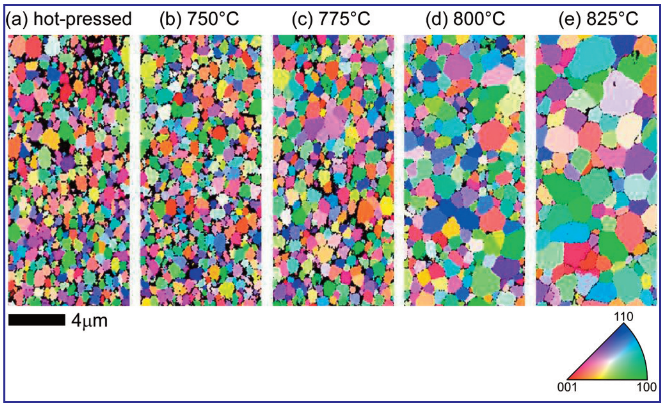

Figure 6. Color coded orientation maps of polycrystalline MgF_2 after (a) hot-pressing and after (b-e) annealing for 1 hour at the temperatures indicated. (By permission of the authors [2] and sponsoring agency – Naval Air Warfare Center AD.)

Optical transmittance measurements were made at several different wavelengths from the polycrystalline MgF_2 samples shown in Figure 6. These results are plotted as a function of grain size in Figure 7.

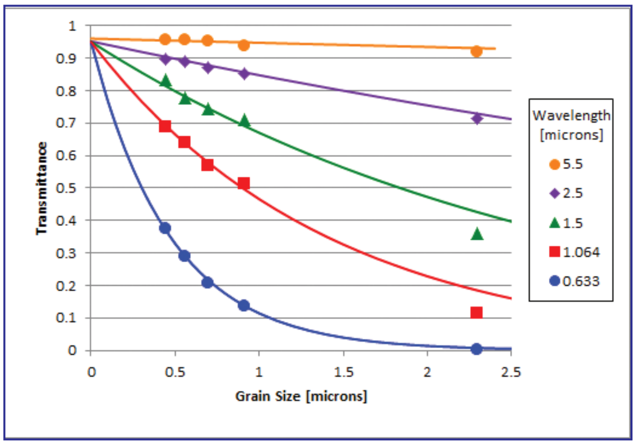

Figure 7. Optical transmittance of polycrystalline MgF_2 as a function of grain size at five different wavelengths. The solid lines are from an analytical approximation [3].

Magnesium Aluminate Spinel

Traditionally, spinels referred to red gemstones but in modern scientific literature it refers more specifically to crystals of Magnesium Aluminum Oxide ($MgAl_2O_4$) or sometimes a class of minerals with a specific chemical formulation and cubic crystal structure. $MgAl_2O_4$ crystals are transparent over a wide range of wavelengths. EDS in the transmission electron microscope (TEM) has been utilized to study the effect of variations in chemical composition across grain boundaries in a fine-grained spinel [10]. Figure 8 shows the microstructure of a $MgAl_2O_4$ after hot-pressing and subsequent annealing. This figure was constructed from EBSD scan data on the sample. The colors of the grains in map correspond to their crystallographic orientation relative to the sample normal and the hue is created by mapping the quality of the corresponding diffraction pattern at each point in the OIM scan to a gray scale.

Analysis of the EBSD data obtained for this sample showed that there was very little preferred orientation of the constituent crystals and that the misorientation at the grain boundaries was random as well. Ting and Lu [11] have studied the role of grain boundaries as well as sub-grain boundaries on the evolution of microstructure in these materials using selected area diffraction in the TEM. EBSD is an ideal tool for expanding the study of grain boundaries in these materials as it can analyze many boundaries relatively easily allowing for statistical analysis of grain boundary misorientation [12].

Figure 9 shows two EDS spectra, one corresponding to a hot-pressed sample and the other to the hot-pressed and annealed sample shown in Figure 7. The spectrum shows that the ratio of Mg/O and Al/O clearly decreases after annealing.

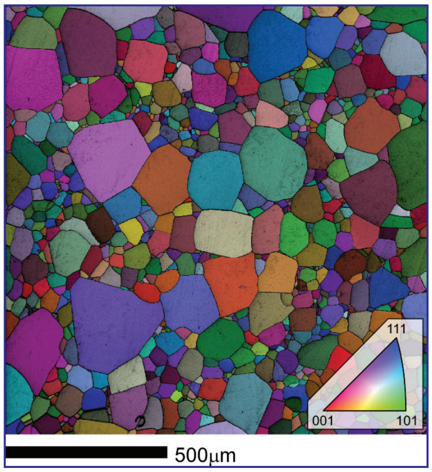

Figure 8. Orientation map overlaid on an intensity map based on EBSD pattern quality on a hot-pressed sample $MgAl_2O_4$ sample.

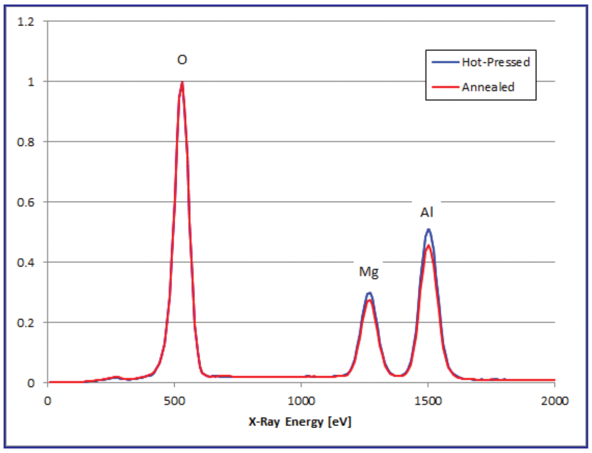

Figure 9. EDS spectra from a hot-pressed sample $MgAl_2O_4$ sample and a hot-pressed and annealed sample.

Alumina

It is interesting to note that texture plays a role on the transmittance performance of ceramic materials [4]. Generally hot-pressed powder compacts do not exhibit much texture as the forming process tends to be isotropic. However, some texture can be observed in these materials. For example, Figure 10 shows the microstructure of a hot-pressed transparent alumina sample accompanied by the corresponding texture in the form of an inverse pole figure (an inverse pole figure shows the preference of specific crystal axes to align with a specific sample direction, in this case the sample normal.) The material has an average grain size of approximately 300 nm. The scan area contains 1650 individual grains. This number of grains should provide a reasonable assessment of the texture [13]. The texture is relatively weak; the highest intensity is nearly two times random for the c-axes to be aligned with the sample normal.

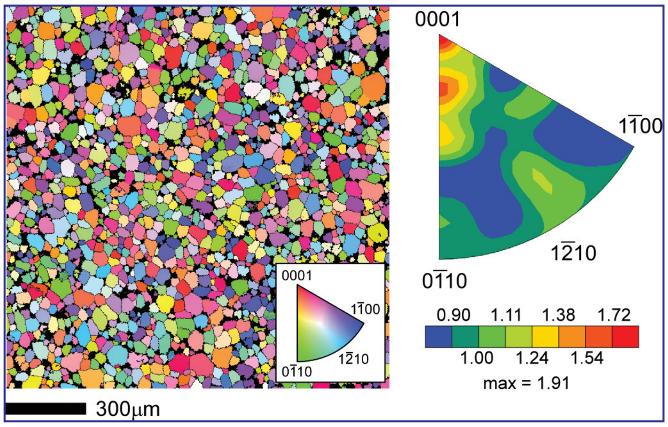

Figure 10. Orientation map and corresponding texture for a hot-pressed Al_2O_3 sample.

Conclusions

There are several new and exciting areas of research in the arena of optical materials, both in developing new materials as well as in new forms of existing materials systems. Understanding both the development of microstructure in these materials and its role in the optoelectronic performance is important for improving their fabrication and performance as well as expanding their application into new fields of technology. The capability of EBSD and EDS characterize different aspects of microstructure makes them important tools for gaining the necessary insight into linking microstructure with properties.

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