Optical band gap of Zn₃N₂ films

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The results of measurements of the optical band gap of Zn_3N_2 films, which crystallize in cubic antibixby te structure (space group: *Ia*3), are presented. The polycrystalline films are prepared by direct reaction between NH₃ and zinc films on quartz substrates kept at 410 °C. Analysis of the thin-film data at higher values of the absorption coefficient is inconclusive with respect to the band-gap nature of the edge. Nevertheless, indirect evidence suggests that the optical gap is probably direct and lies in the neighborhood of 3.2 eV. This value is larger than those of other tetragonal II-V compounds: Zn_3P_2 ($E_g = 1.51$ eV) and Zn_3As_2 ($E_g = 0.93$ eV). The origin of the large band gap of Zn_3N_2 is discussed.

 Zn_3N_3 is a crystal with the cubic antibixbyite structure.¹ The structure is thought of an incomplete cubic close packing of the zinc ions. The zinc atoms occupy three-fourths of the fluorine positions in the CaF₂ structure. Each nitrogen atom has around it four closest zinc atoms. Zn_3N_2 is found in the syntheses² of a filled tetrahedral semiconductor LiZnN which has been proposed as a material with a *direct wide band gap*.³ The band gap of Zn_3N_2 is very likely to be close to the probable band gap (2.6–3.0 eV) of LiZnN.⁴ To our knowledge, the band-gap value of Zn_3N_2 has not been reported. In this paper we present the optical band gap of the cubic phase Zn_3N_2 films.

The Zn_3N_2 films used in this study were prepared by direct reaction between NH₃ and zinc (99.9999% pure). After zinc was evaporated onto a quartz substrate whose thickness is 10 μ m, the Zn film was heated to 410 °C in N_2 flow. The Zn film was subsequently annealed in NH_3 flow at 410 °C for 4 h. The typical x-ray-diffraction pattern consisting of the single phase Zn_3N_2 is shown in Fig. 1. Although some diffraction lines were not observed, it is certain that the film was polycrystalline cubic Zn_3N_2 . The lattice constant was evaluated to be $a = 9.78 \pm 0.01$ Å in good agreement with the previously reported value.1 The thickness and homogeneity of the



FIG. 1. Typical x-ray-diffraction pattern of the Zn_3N_2 film, which crystallizes in the cubic antibixbyite structure with $a=9.78\pm0.01$ Å.

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prepared Zn_3N_2 films were evaluated using the Rutherford backscattering spectrometry (RBS) technique. The RBS measurements⁵ were performed at a scattering angle θ =150° using a silicon surface-barrier detector. Figure 2 shows a typical random spectrum of backscattering yield versus channel number (i.e., energy) for 1.5-MeV ⁴He⁺ ions. This spectrum is also shown in Fig. 2 together with a schematic indication of the separate contributions of each element in the target. The film thickness is about 3000 Å. The slight increase in RBS yields around the 180 channel shows the existence of an oxide at the surface. The spectrum for nitrogen is buried in the RBS spectrum for the quartz substrate. The spatial homogeneity of zinc in depth was confirmed by RBS, except for the slight diffusion into the substrate.

The optical measurements were carried with a similar method to that used for LiInS_2 single crystals⁶ using a scanning spectrophotometer (Shimadzu UV-3101 PC). The optical transmission of Zn_3N_2 films was measured at 300 K using unpolarized light at normal incidence in the photon wavelength range 200–2000 nm. A typical transmission curve is shown as a function of wavelength in Fig. 3. The fundamental absorption edge lies at around 380 nm. The inset shows the absorption coefficient near the absorption edge. Although the presence of additional absorbing centers such as dangling



FIG. 2. Typical RBS spectrum of the Zn_3N_2 film on quartz using 1.5-MeV ⁴He⁺.



FIG. 3. Typical transmission spectrum of the Zn_3N_2 film (thickness t = 3000 Å). The interference effect arising from a quartz substrate is observed over the range 1100-2000 nm. The inset shows the absorption coefficient near the absorption edge.

bonds or accumulated impurities at the grain boundaries is suggested, the band-gap edge is likely to lie at around 3.2 eV. The interference effect in the transmission curve observed over the range 1100-2000 nm arises from the quartz substrate. In order to test the band-gap nature, we plotted two relations,⁷ $\alpha h \nu = A (h\nu - E_g)^{1/2}$ as a direct material and $\alpha h \nu = A'(h\nu - E_g)^2$ as an indirect material (see Fig. 4). Although analysis of the thin-film data at higher values of absorption coefficient is inconclusive with respect to the band-gap nature, the data are likely to obey the relation of directness rather than that of indirectness, because the plot for indirect transitions scarcely shows a linear portion.

The band gap of Zn_3N_2 evaluated in the present study is larger than those of other II-V compounds: Zn_3P_2 $(E_g = 1.51 \text{ eV})$ (Ref. 8) and Zn_3As_2 $(E_g = 0.93 \text{ eV})$.⁹ The phosphide and arsenide are tetragonal¹ with unit containing eight molecules. Each zinc atom is surrounded by a deformed tetrahedron of phosphorus (arsenic) atoms with several Zn-P (As) bond lengths. Each atom of phosphorous (arsenic) has six zinc neighbors. Thus these compounds are composed of covalent bonds with different bond lengths. On the other hand, the nitride is formed from four nearest-neighbor bonds. Therefore the



FIG. 4. Plots to test two relations, $(\alpha h\nu)^2$ vs $h\nu$ as a direct material and $(\alpha h\nu)^{1/2}$ vs $h\nu$ as an indirect material, for the Zn₃N₂ film near the fundamental absorption edge at 300 K.

covalent bond in cubic phase Zn_3N_2 would be much stronger than those of the tetragonal phosphide and arsenide. However, there must be an important difference in the ionicity of the II-V bonds in these compounds. Although the ionicity of a single bond proposed by Pauling,¹⁰ $f_i = 1 - \exp[-(X_A - X_B)^2/4]$, is applied only to tetrahedrally coordinated compounds in an sp^3 hybridized state,¹¹ for qualitative purposes the degree of ionicity would be proportional to $X_A - X_B$, where X_A and X_B are electronegativity of atoms A and B, respectively. Elemental electronegativity X values¹² for Zn, N, P, and As are 0.91(1.6), 3.00(3.00), 1.64(2.1), and 1.57(2.0), respectively. Pauling's values¹⁰ are also given in parentheses. Thus an increase in the ionicity of II-V bonds in these compounds is enhanced by replacing a heavier V element by a lighter one. The large band gap of Zn₃N₂ must be attributed to the larger ionicity of the Zn-N bond.

In conclusion, we found that the optical band gap of the Zn_3N_2 film, which crystallizes in a cubic antibixbyte structure, lies at around 3.2 eV at 300 K. Although analysis of the thin-film data at higher values of the absorption coefficient is inconclusive with respect to the nature of the edge, the band-gap nature is likely to be direct. We propose that the origin of the wide band gap of Zn_3N_2 is attributed to the large ionicity of Zn-N bond.

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