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# Equilibrium-thickness Amorphous Films on $\{1\,1\,\bar{2}\,0\}$ Surfaces of $Bi_2O_3$-doped ZnO

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### Abstract

*Model experiments and thermodynamic calculations revealed that a nanometer-thick liquid/amorphous film is the equilibrium configuration of the* $\{1\ 1\ \bar{2}\ 0\}$ *surfaces of* $Bi_2O_3$*-doped ZnO. In samples equilibrated both above and below the eutectic temperature, bismuth enriched amorphous films were observed. The film thickness is fairly uniform. The average thickness of ninety-seven films formed at 780°C (above the eutectic temperature, 740°C) is 1·54 nm, with a narrow standard deviation of 0·28 nm. In addition, the thickness was found to be independent of firing time or second phase fraction. Therefore, we conclude that the surface film has an 'equilibrium-thickness.' A thermodynamic model is presented. This new observation may have relevance to the understanding and control of surface coatings in ceramics and related properties. © 1999 Elsevier Science Limited. All rights reserved*

*Keywords*: equilibrium-thickness, surfaces, ZnO

## 1 Introduction

Equilibrium-thickness intergranular films have been observed in many ceramic systems, including $Si_3N_4$, $Al_2O_3$, $ZrO_2$, $RuO_2$ and SiC doped with various additives.[1–8] The thickness of the films is on the order of one nanometer, is nearly constant along the boundary, and varies little from boundary to boundary.[1,2] Dihedral angles are nonzero where boundary films interact with glass pockets.

Clarke[8] proposed that the thickness of the intergranular films represents an equilibrium separation between grains. In the simplest form of this model, the total free energy is the sum of van der Waals attractive interaction and a steric (ordering or structural) repulsive interaction, and the film energy has a local minimum (at the equilibrium thickness) where the attractive and repulsive forces balance.

A generalized treatment of the ordering force has recently been presented.[1,2] Films have also been observed at heterophase interfaces.[1–4] In addition amorphous films have been shown to be the equilibrium interfacial phases at Bi-doped ZnO grain boundaries[9] and $TiO_2$–$SiO_2$ hetero-phase boundaries,[3] below the solidus temperature.

Therefore equilibrium-thickness films have been identified in both grain boundaries and hetero-phase interfaces. It was unknown whether similar films can persist on free surfaces. This study shows that surface films with an 'equilibrium-thickness' can exist in the model binary system ZnO–$Bi_2O_3$.

## 2 Experimental Observations

Bismuth-doped zinc oxide powders were prepared by a co-precipitation method.[10] Powders were calcined and then isothermally heated to reach their equilibrium configuration, and air-quenched. Transmission electron microscopy (TEM) specimens were prepared by dispersing the powders ultrasonically in acetone and dropping a small amount of the suspension onto carbon-coated copper grids. High resolution electron microscopy (HREM) was carried out on a Topcon/Akashi EM-002B microscope operating at 200 kV. The bismuth and zinc distributions were mapped using a Fisons/Vacuum Generators HB603 dedicated scanning transmission electron microscopy (STEM) equipped with a Link Systems energy dispersive X-ray (EDX) analyzer.

In ZnO samples saturated with $Bi_2O_3$ and equilibrated at 780°C ($T_{\mathrm{eutectic}} = 740°C$), more than 100 surface amorphous films were observed. One of the typical HREM images is shown in Fig. 1. STEM EDX mapping showed that these films are bismuth enriched (Fig. 2), which is consistent with the fact that the surface films have generally dark contrast in bright field images. Thus, the surface films are not absorbed contamination layers. Since no ion milling

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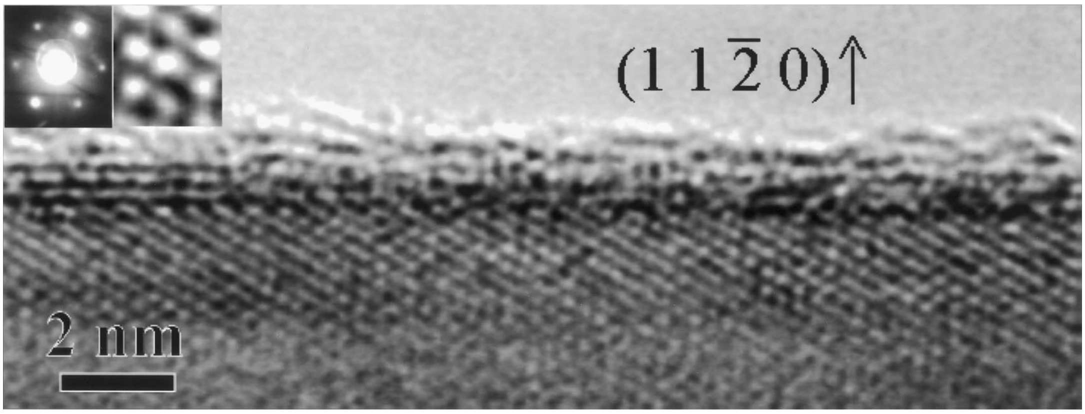

**Fig. 1.** HREM image of an equilibrium-thickness surface film in Bi-doped ZnO equilibrated at 780°C. The insets are the electron diffraction pattern and HREM of a single crystal cell, which indicate that the surface is of $(1\,1\,\bar{2}\,0)$ orientation.

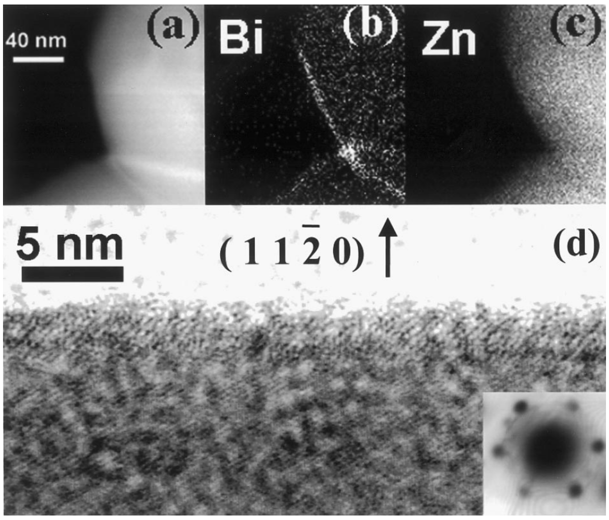

**Fig. 2.** (a) STEM dark field image, (b) Bi map, (c) Zn map, and (d) HREM of a surface amorphous film in Bi-doped ZnO equilibrated at 780°C.

was involved in the TEM sample preparation, they are also not artifacts due to ion thinning. However, under irradiation by 200 kV electrons ($\sim 10^{23}$–$10^{24}$ $e/m_2$ fluence), these surface amorphous films decompose after a few minutes into nanometer-sized crystalline clusters. It is therefore necessary to minimize exposure during HREM in order to characterize the initial as-fired state of the surfaces.

Statistically, amorphous films only form on a small fraction of surfaces. Seventy five such surfaces were identified to be of $\{1\,1\,\bar{2}\,0\}/\{110\}$ orientation using electron diffraction. Figure 3, taken with the electron beam along the [0001] crystalline zone axis, clearly shows this anisotropy. Amorphous films are observed only on the $\{1\,1\,\bar{2}\,0\}$ surfaces, and not on the $\{1\,\bar{1}\,0\,0\}$ or other higher index surfaces.

The film thickness is fairly uniform along the surface (Fig. 4). The average thickness of 97 films

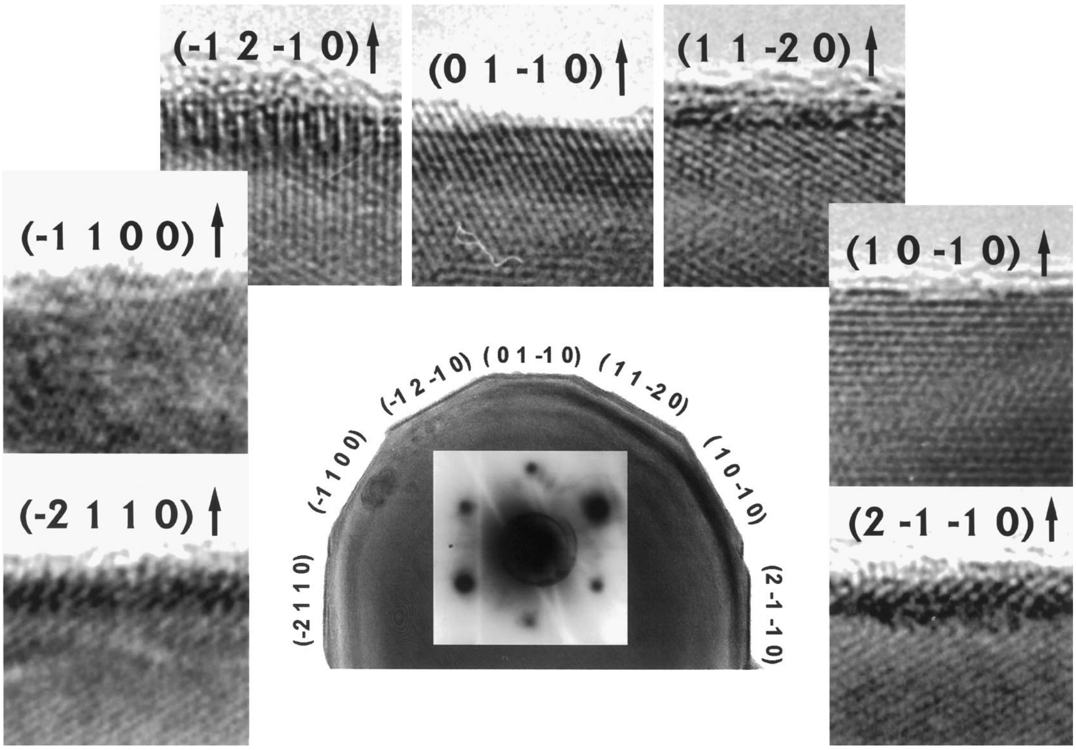

**Fig. 3.** In Bi-doped ZnO equilibrated at 780°C: bismuth-enriched films form on $\{1\,1\,\bar{2}\,0\}$ surfaces, but not on $\{1\,\bar{1}\,0\,0\}$ surfaces.

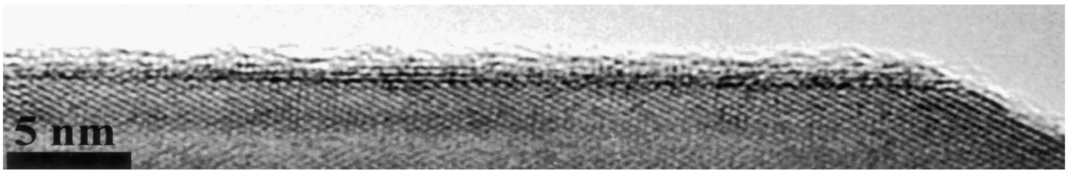

**Fig. 4.** A surface amorphous film in Bi-doped ZnO equilibrated at 780°C with nearly constant thickness along the surface.

which could be imaged clearly is 1·54 nm, with a standard deviation of 0·28 nm. In addition, the thickness is independent of firing kinetics and the amount of excess secondary phase. The average thickness of surface films in ZnO-0·58 mole% $Bi_2O_3$ powders heated at 780°C for 1, 2 and 3 h respectively is 1·54, 1·52 and 1·47 nm respectively, the difference being well within the standard deviation of each measured distribution (Fig. 5(a)). At a higher doping level of 1·68 mole% (780°C, 1 h) the average film thickness was measured to be 1·56 nm, which is again well within the standard deviation of the thickness (Fig. 5(b)). Since the solid solubility of $Bi_2O_3$ in ZnO is less than 0·06 mole%, doping levels of 0·58 and 1·68 mole% both represent saturated samples in which the chemical potentials are the same while the secondary phase fractions vary. The fact that the surface film thickness is constant again suggests that it is an 'equilibrium thickness.'

These surface films were also found to form below the eutectic temperature. In samples isothermally heated at 700°C for 10 h, 12 surface films were identified. The film thickness ranges from 0·85 to 2·2 nm, with an average of 1·4 nm. Five such surfaces which could be clearly characterized were identified to be also of $\{1\,1\,\bar{2}\,0\}$ orientation.

## 3 Theoretical Modeling and Discussion

These films are most likely the free-surface counterpart of the well-known equilibrium thickness intergranular films in ceramics. A preliminary thermodynamic model for surface films based on Ackler's model for intergranular films[1,2] is described as follows. For a surface liquid film of thickness $h$ on a crystal, assumed for simplicity to be uniform in composition and free of electrostatic (space charge) interactions, the total free energy of the film consists of an ordering interaction and the van der Waals interaction (dispersion force). In a mean field approach, the ordering interaction can be expressed as[1,7]

$$\sigma = \int_0^h [v^2\phi(x)^2 + \varepsilon^2(\nabla\phi(x))^2]\mathrm{d}x + \gamma_{qv}(\phi(h)). \quad (1)$$

where $\phi(x)(0 < x < h)$ is defined as the spatially varying order parameter in the film, while $v$ and $\varepsilon$ are thermodynamic coefficients characterizing the variation in volumetric and interfacial energy with the order parameter and its gradient, respectively. The first term is the integral of volumetric and gradient energies across the film.[1,7] The second term, $\gamma_{qv}(\phi(h))$, is introduced to characterize the interfacial energy of the liquid/vapor interface as a function of its order parameter. As the film thins, greater order is imposed on the free surface, raising its energy and providing a repulsive force against thinning. This term can be expanded in a series:

$$\gamma_{qv}(\phi(h)) = \gamma_{qv}(0) + \Delta\gamma\phi(h)^2 + \ldots \quad (2)$$

where $\gamma_{qv}$ and $\Delta\gamma$ are constants. By definition, $\gamma_{qv}(0) = \gamma_{lv}$ and $\gamma_{qv}(1) = \gamma_{cv}$, where $\gamma_{lv}$ and $\gamma_{cv}$ are the interfacial energies of liquid/vapor and crystal/vapor interfaces respectively. These relations imply that $\Delta\gamma = \gamma_{cv} - \gamma_{lv}$. It is further assumed that $\Delta\gamma$ is positive ($\gamma_{lv} < \gamma_{cv}$) and the crystal surface (at the crystal/liquid interface) can impose some structure on the immediately adjacent liquid, which gives the boundary condition '$\phi(0) = a$.' ('$a$' being the order parameter of the liquid at the crystal/liquid interface.) The ordering force can be obtained by minimizing:

$$\sigma(h) = \int_0^h [v^2\phi(x)^2 + \varepsilon^2(\nabla\phi(x))^2]\mathrm{d}x + \Delta\gamma\phi(h)^2, \quad (3)$$

subject to the boundary conditions:

$$\phi(0) = a, \phi(h) = \text{arbitrary}. \quad (4)$$

The second boundary condition is a statement that the order parameter at liquid/vapor interface, $\phi(h)$, is allowed to vary freely (but with an energy penalty of $\Delta\gamma\phi(h)^2$) in order to minimize the total energy. The solution is

$$\sigma(h) = a^2\varepsilon v\left[\frac{1}{\tanh(\frac{hv}{\varepsilon})} - \frac{\csc h(\frac{hv}{\varepsilon})}{\cosh(\frac{hv}{\varepsilon}) + \frac{\Delta\gamma\sinh(h\gamma/\varepsilon)}{\varepsilon\gamma}}\right]. \quad (5)$$

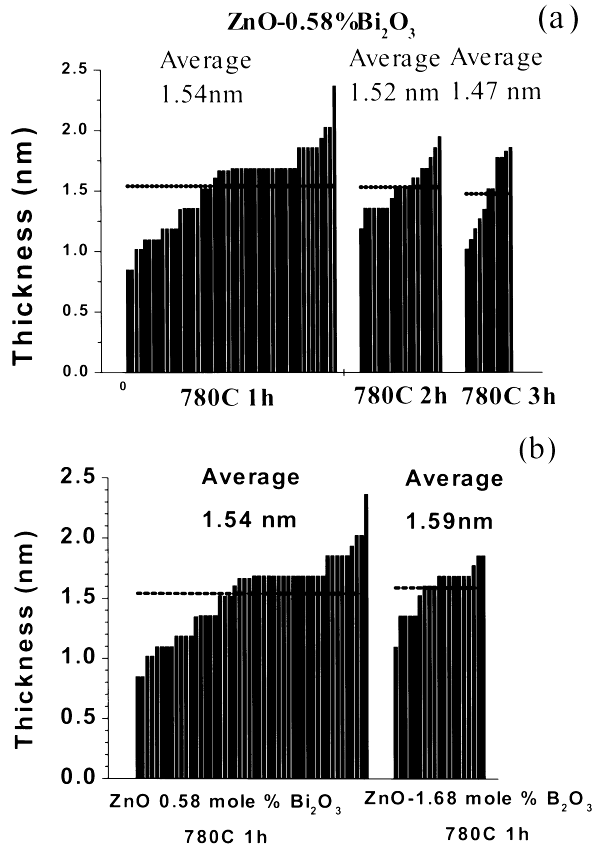

**Fig. 5.** The thickness of surface films in (a) ZnO–0·58 mole% $Bi_2O_3$ powders heated at 780°C for 1, 2 and 3 h, respectively; and in (b) ZnO powders doped with 0·58 mole% $Bi_2O_3$ and 1·68 mole% $Bi_2O_3$, respectively, and heated at 780°C for 1 h. Each bar in the chart represents one surface film.

The total film energy (as a function of thickness) was then taken to be the sum of $\sigma$ $(h)$ and the van der Waals interaction:

$$E(h) = \sigma(h) + \frac{-A}{12\pi h^2} \qquad (6)$$

Note that for the present system in which a high dielectric constant film is on a lower dielectric constant substrate, the van der Waals term acts to thin the film ($A$ is positive.).

Figure 6 shows the calculated energy versus thickness curves using some reasonable thermodynamic parameters estimated using Refs 1 and 2. The results indicate that if the $\{11\bar{2}0\}$ crystal surface imposes sufficient order on the adjacent liquid, (in other words, if $a(=\phi(0))$ is greater than a critical value $a_c$) a local energy minimum arises. Under these conditions, an equilibrium-thickness liquid film can exist on the surface.

Below the eutectic temperature, it is presumed that the volumetric free energy term is represented by that for amorphization of the film composition from its corresponding crystalline form. Nonetheless, if the crystal imposes strong order on the adjacent glass, the increase of volumetric free energy due to amorphization can be more than compensated by the reduction in total interfacial energy if the structure of film remains amorphous rather than crystallizing. That is, interfacial energy can stabilize 'solid-state amorphization' of the film.

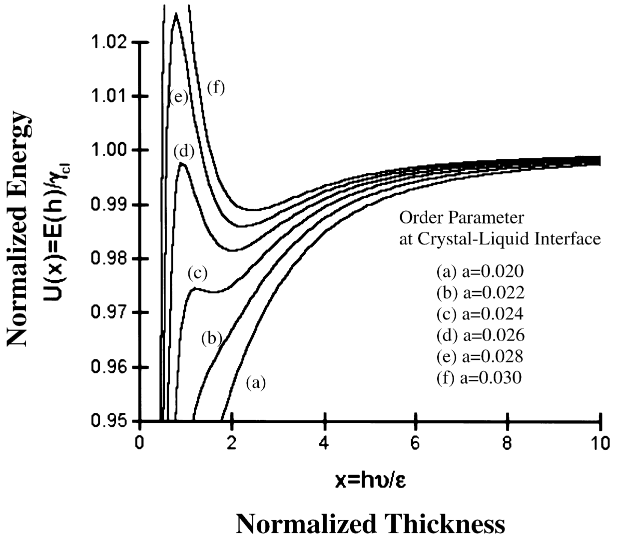

**Fig. 6.** Calculations of the excess energy of a surface film versus its thickness. The parameters used are: $\Delta\gamma/\varepsilon\nu = 3$, $A\nu/\varepsilon^3 = 0.0001$, $a = 0{\cdot}020$, 0·022, 0·024, 0·026, 0·028, and 0·030 respectively. The surface film has an equilibrium thickness if $a \geq 0{\cdot}024$.

## 4 Conclusion

Bismuth-enriched, equilibrium-thickness, amorphous films have been observed on the $\{11\bar{2}0\}$ surfaces of bismuth-doped zinc oxide. These films are considered to be the free surface counterpart of the equilibrium-thickness intergranular films that have been widely observed in ceramics. A thermodynamic model is presented that indicates that this equilibrium-thickness surface film exists due to two conditions: (1) The $\{11\bar{2}0\}$ crystal surface of ZnO imposes a fairly strong order on the immediately adjacent bismuth-enriched liquid layer; (2) The $\{11\bar{2}0\}$ crystal surface energy is greater than that of the liquid free-surface in addition to the presence of a positive Hamaker constant.

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