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Heteroepitaxy of Hafnium Diboride on a Hafnium(0001) Single Crystal Surface

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Transition-metal carbides, nitrides, and borides are metallic hard materials with current and potential applications as thin-film coatings.[1] While titanium nitride and tungsten carbide are already widely used as coatings for cutting tools, titanium diboride is actually harder than either material. While the borides share many physical properties with nitrides and carbides, the MB_n borides with $n \geq 2$ adopt unique structures[2] that have no analogues among other compounds. The unique structures of the borides suggests that heterostructures can be formed with them that are not possible with carbides or nitrides. A case in point is provided by the special relationship between the structures of Ti, Zr, and Hf and their corresponding diborides. These group IVA metals have an hcp structure with atoms of the (0001) surfaces occupying points of a simple two-dimensional triangular lattice. Their diborides have a hexagonal structure that consists of alternating metal and boron layers with the metal atoms also occupying points of a two-dimensional triangular lattice.[2] Figure 1 shows the three topmost atomic layers of the (0001) surfaces of Hf and HfB_2. The lattice constants within the (0001) metal layers of the metals and their diborides are very similar with the best lattice matching for Hf and HfB_2 with lattice constants of $a = 3.197$ and 3.143 Å, respectively.[2,3] As shown in Table 1 for Hf and HfB_2, the similarities in structure are in contrast to the markedly different physical properties of the two materials. The lattice mismatch of 1.7% for Hf and HfB_2 compares with lattice mismatches of 2.6 and 1.9% for the Ti/TiB_2 and Zr/ZrB_2 pairs. These factors were the basis for the work reported here on the growth and characterization of epitaxial thin films of HfB_2(0001) on a Hf(0001) substrate.

Although there have been no previous reports of epitaxial growth of borides on metals in general or of HfB_2 on Hf in particular, there have been several studies of the deposition of nonepitaxial diboride thin films.[4−10] Group IVA metal diborides have been prepared by evaporation,[5] sputtering,[6] or chemical vapor deposition (CVD) utilizing the reaction of the corresponding metal chlorides with diborane[7] or BCl_3 and hydrogen.[8] Metal tetraborohydride based precursors are also used for diboride CVD.[9] A new synthetic method involving the high-temperature (>1900 °C) pyrolysis of the metal oxide/boron containing polymer dispersion was recently proposed.[10] A variety of amorphous and polycrystalline diboride films have been obtained by these techniques.

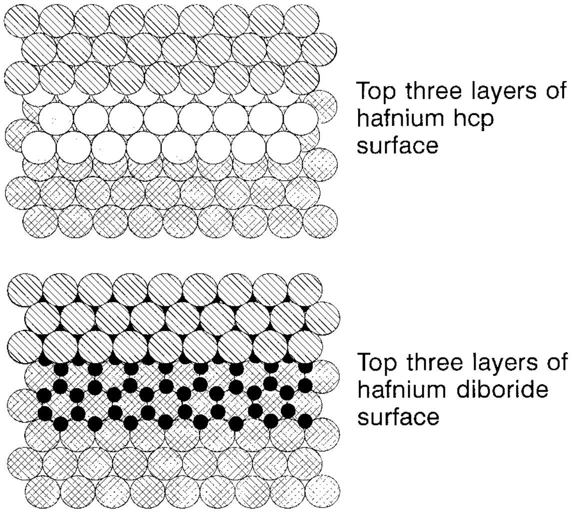

Figure 1. Comparion of three layers of Hf (0001) and HfB_2(0001) showing that the topmost atomic layer of each surface consists of Hf atoms arranged in a close-packed triangular lattice.

Table 1. Physical Properties of Hafnium and Hafnium Diboride[a]

	hafnium	hafnium diboride
density, g/cm^3	13.28	10.50
melting point, K	2467	3643
crystal structure: hcp, Å	$a = 3.19$, $c = 5.05$	$a = 3.143$, $c = 3.479$
resistivity at 298 K, $\mu\Omega$ cm	33.7	8.8

[a] All values are from ref 3, except for the lattice constants of HfB_2, which are from ref 17.

The films were grown in two separate stainless steel ultrahigh vacuum (UHV) chambers with base pressures $<1 \times 10^{-10}$ Torr, which are described in detail elsewhere.[11,12] The HfB_2 film growth was monitored within the UHV chambers by X-ray photoelectron spectroscopy (XPS) and low-energy electron diffraction (LEED) and was characterized with X-ray diffraction (XRD) after removal from the UHV environment. The Hf(0001) single crystal was purchased from Metal Crystals and

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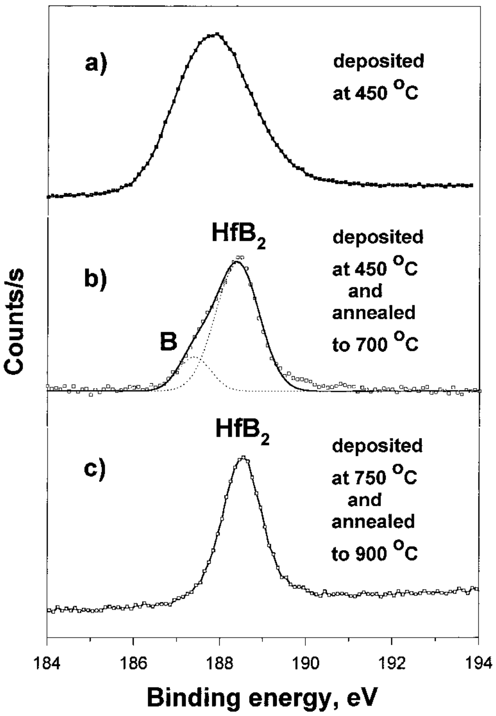

Figure 2. XPS spectra of the B(1s) region of (a) a film deposited at 450 °C; (b) a film deposited at 450 °C and annealed to 700 °C; (c) a film deposited at 750 °C.

Oxides, Ltd., and was cleaned by multiple cycles of Ar$^+$ ion sputtering and annealing to 800 °C. The clean crystal exhibited a sharp 1 × 1 unreconstructed LEED pattern, and the only impurity detected by XPS was oxygen (~1% of a monolayer, according to the standard atomic sensitivity factors[13]). Although zirconium is a common impurity in hafnium, the absence of the Zr 3d$_{5/2}$ XPS peak at a binding energy of 181 eV indicates that at least the surface region was relatively free of zirconium. The crystal was heated to the deposition temperature and exposed to 5×10^{-5} Torr of a 1% diborane in argon mixture. The XPS analysis of the HfB$_2$ films was performed using a VG CLAM2 analyzer and a Mg anode X-ray source. The spectrometer was calibrated using both Au 4f$_{7/2}$ (84.00 eV) and Ag 3d$_{5/2}$ (368.27 eV) transitions as the reference binding energies, assuming a linear dependence of the correction shift on binding energy.[14] The position of the Hf 4f$_{7/2}$ peak for all experiments was 14.3 ± 0.1 eV, which is close to reported values for polycrystalline HfB$_2$ samples and coatings[15] and elemental hafnium.[16] Our interpretation of these HfB$_2$ thin-film results was greatly aided by parallel studies of a HfB$_2$(0001) single-crystal surface.[12] The diboride films were free of all contaminants except for oxygen, the amount of which was comparable to the amount of oxygen on the nominally clean Hf(0001) and HfB$_2$(0001) surfaces.

Figure 2 shows XPS spectra of the B(1s) region for films deposited under various conditions. A 3 h deposition at 450 °C with a diborane pressure of 5×10^{-5} Torr gave a film with one broad B(1s) peak at a binding energy of 187.8 eV (Figure 2a). This film is boron-rich with a Hf:B ratio of 1:3. The B(1s) binding energy is a sensitive indicator of the boron chemical state, and the large width of the B(1s) peak in Figure 2a is attributed to the presence of a mixture of boron chemical states. No diffraction spots were observed with LEED for the film of Figure 2a, indicating the absence of long-range order. Annealing the film to 700 °C caused a decrease in the B(1s) peak intensity and change in line shape (Figure 2b). Peak-fitting yields two different boron chemical states. The first, at a binding energy of 187.7 eV is assigned to elemental boron based on a similar value obtained for elemental boron.[11] However, the close agreement may be fortuitous given the subtleties involved in assigning precise binding energies for semiconductors such as boron. The second peak in Figure 2b at 188.4 eV is assigned to the diboride based on comparison with the B(1s) binding energy of 188.4 eV for the HfB$_2$(0001) single-crystal surface.[12] Diffusion of the excess boron into the bulk of the hafnium crystal is most likely responsible for the intensity decrease between parts a and b of Figure 2. A diffuse (1 × 1) LEED pattern was observed after annealing. This LEED pattern is attributed to a crystalline diboride film since it was observed after XPS indicated that the substrate had reacted with the initially disordered boron layer to form HfB$_2$. Annealing the film to 900 °C eliminates all nonstoichiometric boron from the surface, which in turn gives only a diboride B(1s) peak at 188.4 eV. Figure 2c shows XPS results for a film deposited at 750 °C and annealed at 900 °C. Clearly, the spectrum of Figure 2c shows that only the HfB$_2$ phase is present on the surface. The Hf/B ratio was 1:2 and a sharper (1 × 1) LEED pattern than for the film of Figure 2b was observed. A sharp (1 × 1) LEED pattern is also obtained from the HfB$_2$(0001) single-crystal surface. The observation of a B(1s) binding energy and B(1s):Hf(4f$_{7/2}$) peak area ratio identical with that from a HfB$_2$(0001) single crystal is compelling evidence for the formation of a HfB$_2$ film on the substrate. The observation of a (1 × 1) LEED pattern as also observed for both the Hf(0001) and HfB$_2$(0001) surfaces[12,17] indicates that the film is epitaxial. The thickness of the film was not determined directly but can be estimated from the fact that a deposition time of 6 h gave a HfB$_2$ layer just thick enough for the Hf:B ratio to reach 1:2 and the B(1s) peak to correspond to that of HfB$_2$. This implies that the thickness of the film is on the order of 2−3 times the electron escape depth, which is about 2 nm for Hf and HfB$_2$.[18]

The XRD results shown in Figure 3 were obtained on the thin film that yielded the XPS spectrum of Figure 2c. In addition to the intense Hf(0002) peak from the substrate, the next two largest peaks are assigned to HfB$_2$(0001) and HfB$_2$(0002).[19] In an XRD analysis of polycrystalline HfB$_2$, the (10$\bar{1}$1) reflection was found to be most intense.[19] The absence of peaks due to HfB$_2$ planes not parallel to the [0001] direction confirms the epitaxial nature of the film. In addition, small peaks

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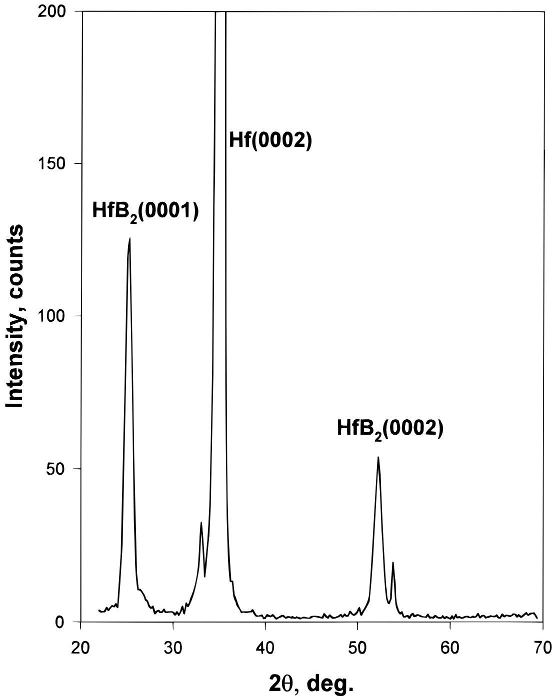

Figure 3. XRD analysis of the HfB_2 film deposited at 750 °C and annealed to 900 °C.

at 33.64° and 54.54° are also seen. Although these minor peaks are in reasonably good agreement with reported values[20] for the (011) and (311) reflections from orthorhombic HfB, such a hafnium monoboride phase is not well-documented. In addition to the XPS, LEED, and XRD results, the epitaxial nature of the film is supported by the angular dependence of the Hf(4f)/B(1s) peak area ratio. Such ratios often undergo oscillations due to photoelectron diffraction. A HfB_2 film deposited under conditions that gave the best crystalline film (as indicated by LEED and XPS) yielded angular plots identical with those from the HfB_2(0001) single-crystal surface. Furthermore we have characterized the chemical reactivity toward CO and O_2 of the Hf(0001), HfB_2(0001), and HfB_2/Hf(0001) surfaces. We find that although the Hf and HfB_2 single-crystal surfaces display significantly different surface chemistry, the thin HfB_2 film on Hf(0001) shows the same chemical behavior as the HfB_2(0001) single-crystal surface. A full description of these other results will be published elsewhere.[12] All of these observations provide unambiguous evidence for the epitaxial growth of HfB_2 on Hf(0001).

Further work will be required before any assessment of the suitability of these epitaxial films for hard coatings or other applications can be made. Since only B is deposited on the Hf substrate in the method used here, the thickness of the films will be limited by diffusion of Hf through the HfB_2 layer. However, there is no reason to expect that much thicker epitaxial films cannot be grown via a precursor gas that contains both Hf and B, as have been used to grow nonepitaxial films. A thick epitaxial film of a metallic hard material such as HfB_2 may display unique and superior properties as a hard coating. Experiments on the growth and characterization of the macroscopic properties of HfB_2 epitaxial films of thicknesses on the scale of several microns are planned for the near future.

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