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Surface modification of chemically vapor deposited diamond for producing adherent thick and thin film metallizations for electronic packaging

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In order to make chemically vapor deposited diamond (CVDD) substrates amenable to surface metallization without significant reduction in thermal conductivity, very thin alumina films were grown on diamond by vapor deposition of Al in oxygen atmosphere, followed by very low-temperature annealing in oxygen. A Cr interlayer initially deposited on CVDD prior to alumina deposition was found to lead to excellent adhesion between the substrate and the deposit. The alumina films were characterized by scanning and transmission electron microscopy as well as Auger electron spectroscopy. © *1996 American Institute of Physics*. [S0003-6951(96)02621-6]

Diamond is an ideal substrate material for electronic packaging because of its excellent thermal conductivity, high electrical resistivity, and low dielectric constant.¹ However. diamond is difficult to metallize because of two reasons: (1) The surface of diamond is relatively inert, making it difficult for common, non-carbide forming, metallizations with high electrical conductivity, e.g., Au or Cu, to adhere to it; and (2) its thermal expansion coefficient is very small ($\sim 1-2$ $\times 10^{-6}$ /K), resulting in large interfacial residual stresses between the substrate and the metallization. As a result, traditional approaches^{2,3} to metallize diamond have utilized less electrically conductive, but carbide-forming metals (W, Mo, Nb, or Ti) with smaller thermal expansion mismatch with diamond than Au or Cu, as either (1) the final metallization, or (2) an interlayer between Au or Cu metallizations and diamond. The first approach results in a metallization with less than ideal electrical properties, whereas the second approach requires the interlayer to be patterned identically to the final metallization, which in practice precludes this approach from being used for conventional thick film processes. This letter discusses a novel method to circumvent these limitations by producing a very thin, well-bonded layer of an electrically insulating material of good dielectric strength (alumina) on chemically vapor deposited diamond (CVDD) substrate, such that the thermal conductivity of the treated substrate is not degraded by more than 5% relative to that of the untreated substrate. This allows the treated diamond surface to be metallized using all conventional thin and thick film processes currently in use industry-wide for alumina packages.

The choice of alumina as a surface layer to render CVDD metallizable was based on the following considerations. Alumina has high electrical resistivity $(10^8 - 10^9 \ \Omega \ \text{cm})$, low dielectric constant (8.5), a coefficient of thermal expansion $(7 \times 10^{-6}/\text{K})$ between those of diamond and most metals, is extremely stable chemically and is easily metallizable using currently used techniques. Although alumina has a low thermal conductivity ($K \sim 25$ W/m K), its deleterious effects on the thermal conductivity of the package can be minimized by keeping the alumina layer thickness very small. For instance, a simple one-

In the present work, an alumina layer was produced on a CVDD substrate using a 20-50 nm thick carbide-forming metal (Cr) as an adhesion-enhancing interlayer. Cr was deposited on CVDD by vacuum evaporation at a base pressure of 10^{-7} Torr. Subsequently, a 100–200 nm layer of alumina was deposited by reactive evaporation of Al and 99,99% pure oxygen at a total chamber pressure of 10^{-4} Torr. The substrate was maintained at 575-675 K during deposition. A postdeposition annealing treatment (600 K for 24 h) was carried out in oxygen atmosphere after backfilling the deposition chamber with oxygen to a pressure of \sim 500 Torr. This approach produced a continuous, fine grained, alumina film which adhered strongly to the CVDD substrate. Attempts in separating the films from the substrates by using a replicating acetate tape (and a conventional scotch tape) were unsuccessful and the alumina film could not be removed, demonstrating that the films are quite adherent to the substrate.



FIG. 1. Microstructure of the alumina film deposited on a 20 nm Cr interlayer. This film was deposited on cleaved single-crystal sodium chloride, which was subsequently dissolved in water to separate the film from the substrate. Bright field image shows fine 3-10 nm sized grains. The corresponding SADP, shown as an inset, reveals that the film consists of numerous ultrafine, misoriented γ -Al₂O₃ crystallites. The sharp rings correspond to the following Miller indices starting from the innermost: (220), (311), (400), (511), and (440).

dimensional heat transfer calculation reveals that the through-thickness thermal conductivity of a 200 μ m thick diamond of K=1500 W/m K drops by less than 3% on being coated with a 100 nm thick layer of alumina.

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FIG. 2. Appearance of 125 nm thick surface alumina layer produced on a CVDD substrate with a 50 nm thick Cr interlayer.

Films for TEM studies were produced on a freshly cleaved (100) surface of NaCl under conditions identical to those used for deposition on CVDD, so that the films could be easily separated from the substrate for TEM observations. The film was then characterized by transmission electron microscopy (TEM), energy dispersive x-ray spectroscopy (EDS), scanning electron microscopy (SEM), and Auger electron spectroscopy (AES).

Figure 1 shows a bright field TEM image of the alumina film deposited on a Cr interlayer and the corresponding selected area diffraction pattern (SADP) is shown as an inset. It is observed that the film is nanocrystalline, with the crystallite size ranging from 3 to 10 nm. The sharp, somewhat spotty, rings in the SADP correspond exactly to reflections from γ -Al₂O₃ and confirm that the film is largely crystalline,⁴ with negligible amorphous component. The nature of the alumina films was further confirmed by EDS and AES studies. Figure 2 shows a SEM image of the surface of the alumina film produced on CVDD (deposited on silicon) using the above technique. It is observed that some of the surface crystallites have grown to about 0.2–0.3 μ m due to rapid surface diffusion during the postdeposition heat treatment, although the underlying layer was nanocrystalline (Fig. 1). Figure 3, which is an Auger electron spectrum from the surface of the film, clearly shows two peaks, one corresponding to oxygen at 504 eV, and the other corresponding to aluminum at 1384 eV. The detailed structure of the Al peaks in Fig. 3 was found to be identical to that from a pure



FIG. 3. Auger electron spectrum from the surface of the film deposited on CVDD with a Cr interlayer, clearly showing two peaks—one corresponding to oxygen at 504 eV, and the other corresponding to aluminum at 1384 eV. Details of the Al peak are consistent with the Al peak from a pure Al_2O_3 standard (Ref. 5) and is distinct from the peak from unreacted aluminum.



FIG. 4. Auger depth profile through an \sim 120 nm alumina film deposited on a 50 nm Cr interlayer on a CVDD substrate. For reference, thicknesses where known, are indicated along with sputter time on the abscissa.

 Al_2O_3 standard,⁵ confirming that the film is alumina. Spectra collected after sputtering to different depths of the film were found to be identical, suggesting that a uniform layer of alumina was present on the CVDD samples studied here.

Figure 4 shows an Auger depth profile through the alumina and Cr films deposited on CVDD. The Al/O ratio is observed to be relatively constant until about 100 nm from the surface (sputter time of ~5 min), in agreement with the TEM results, which showed the layer to be γ -Al₂O₃. Significant interdiffusion is observed to have occurred between Cr and Al/O. Furthermore, Cr and C from the underlying CVDD are observed to have interdiffused, and appear to have reacted as well. The prominent O signal near the Cr/C interface is presumed to be due to the diffusion of O adsorbed on the CVDD surface into the Cr layer. The interdiffusion zones between Al₂O₃ and Cr and between Cr and C result in strong chemical bonding between Al₂O₃, Cr, and the CVDD layers, and is responsible for the excellent adhesion of the Al₂O₃ film to the substrate.

Thus, the above surface treatment yields a very thin, ultrafine grained, adherent alumina surface layer on CVDD substrate. Since the surface layer is alumina, which is widely used as a substrate material for electronic packaging, the CVDD substrate, treated as above, is easily metallizable by a number of thin and thin film techniques, using existing technology.

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⁴JCPDS Powder Diffraction File, Card No. 10-425.

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