JOURNAL OF THERMOPHYSICS AND HEAT TRANSFER
Vol. 8, No. 2, April–June 1994

Evaluation of Nonmetallic Coatings and Films for Thermal Control Applications

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An evaluation of the thermophysical and tribological properties of nonmetallic coating materials has been conducted in order to determine which materials are most suitable for thermal enhancement applications. These nonmetallic materials consist of oxides, carbon-based coatings, ceramics, and polymer-based coatings. The thermal conductivity, mechanical, electrical, and tribological properties have been summarized for comparison. Among the oxides, beryllia (BeO) was selected as a potential coating because of its high thermal conductivity in comparison to other oxides. Anodic coatings processed at room temperature result in soft coatings which may lead to improved heat transfer. Carbon-based coatings, such as polycrystalline diamond or diamond-like films, offer excellent thermophysical and tribological properties which makes them attractive as coatings. Ceramics generally exhibit excellent structural and thermal capabilities at high temperatures, however, they are extremely hard and prove to be more suitable for thermal isolation applications. Polymer-based coatings have excellent properties for environmental applications and provide good dimensional and structural stability over a wide range of temperatures.

Introduction

THE power requirements for modern microelectronics systems are increasing due to greater circuit densities on very large scale integration (VLSI) devices. As a consequence, greater capacities for heat dissipation become paramount for reliable operation of these systems, particularly for standard electronic module (SEM) applications. As heat densities approach 100 W/cm^2 and beyond, the efficient removal of this heat must be investigated.

One factor that can contribute to the removal of heat from microelectronic devices is an increase in the contact conductance at junctions. The choice of interstitial material for a particular application is governed by such factors as contact pressure and temperature, environmental conditions, and the degree to which it is desired to reduce or enhance heat flow across the junction. Various control materials are available, and these can be classified by their molecular compositions[1] which have been categorized as: greases and oils, metallic foils and screens, composites and cements, and surface treatments.

At the microelectronic device level, greases and oils can easily be applied to the backside of the device, or the device may be engulfed in the oil or grease to provide maximum contact area. Care must be taken, however, in the selection of molecular composition (antioxidant) to prevent corrosion mechanisms from occurring which will lead to electrical failures. At the electronic packaging level, greases and oils may leak from the joint or evaporate with time. Metallic foils and screens are effective at increasing contact conductance, however, improper placement in the joint can lead to an actual decrease in conductance caused by misalignment or wrinkling of the foil or screen. Metallic foils and screens may be impractical at both the device and packaging levels due to the fact that all chip interfaces must be under equal contact pressures. Composites and cements are generally used for thermal insulation, whereas metallic surface treatments are mainly used to improve contact conductance. Surface treatments such as coatings and vapor-deposited films, however, are more permanent than greases and oils and may be suitable for applications involving device coatings and/or sliding contact between two components. Therefore, surface treatments have a broader applicability.

A thorough search of the literature was undertaken to identify those investigations containing data and predictions for the thermal conductance of coated nonmetallic contacts. Four categories of nonmetallic coating materials were identified: 1) oxides, 2) carbon, 3) ceramics, and 4) polymer-based. The results of this investigation are summarized, and the predictions are then analyzed against available data where possible. A more detailed summary of this investigation was reported by Marotta et al.[2]

Literature Review

An attempt has been made to compare contact conductance data from all published data for metallic coatings,[3] however, a similar comparison of nonmetallic (such as diamond and ceramic films, oxide, and anodic) coatings has not been made. Studies of nonmetallic coatings are limited, although thermophysical and tribological data exist from which engineering judgements can be made, possibly leading to enhanced thermal contact conductance and environmental stability. This review is divided into four sections: 1) oxide/anodic films, 2) carbon-based materials (tetrahedral bonding), 3) ceramic coatings, and 4) surface treatments such as impregnated polymer coatings.

Oxide Coatings

Yip[4] developed a prediction for the contact resistance of oxidized metal surfaces, noting that oxides are much less ductile than most light metals, and their presence decreases the actual contact area. Oxidation film thickness of aluminum alloys vary from 0.003 to 0.3 μm (0.12–12 μin.) when such metals are exposed to air at various humidities. Magnesium and its alloys exhibit a buildup of magnesium hydroxide at a rate of 0.01 μm (0.4 μin.) per year when exposed to humid air. Yip conducted experiments using specimens of 6061-T6 aluminum alloy with average rms surface roughnesses of 1.5 and 6.6 μm (59 and 260 μin.), and an assumed oxide thickness

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Presented as Paper 92-2849 at the AIAA 27th Thermophysics Conference, Nashville, TN, July 6–8, 1992; received Nov. 16, 1992; revision received Aug. 4, 1993; accepted for publication Aug. 13, 1993.

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of 0.075 μm (3 μin.). The contact resistance increased by a factor of 9 for a pair of surfaces with roughnesses of 1.5 μm (59 μin.), and by a factor of 2 for a pair of surfaces with roughnesses of 6.6 μm (260 μin.).

Mian et al.[5] examined the contact resistance of oxide films on samples of mild steel (EN3B). They tested specimens that were lapped flat and then sandblasted to a roughness of 0.084 μm (3.3 μin.). The contact resistance was doubled when the ratio of total oxide film-thickness-to-surface-roughness was approximately equal to 4, but increases in the ratio beyond this value did not significantly increase the contact resistance. The film thickness, rather than the roughness, was the dominant variable affecting the resistance. They correlated the entire population of experimental data and demonstrated that it agreed reasonably well with the analysis of Yip.[4]

Al-Astrabadi et al.[6] developed a theoretical prediction for the contact resistance of oxidized, nominally flat, randomly rough metallic surfaces. The assumptions regarding the nature of the microcontacts are analogous to those later described by O'Callaghan et al.[7] Al-Astrabadi et al.[6] noted that an oxide is, in general, harder and less ductile than its parent metal, and concluded that the formation of oxides tends to reduce the true metal-to-metal contact for freshly assembled joints. They conducted experiments to verify their theory using mild steel (EN3B) specimens with surface roughnesses ranging from approximately 0.12–2.0 μm (4.7–79 μin.), asperity slopes between 0.04–0.19 rad, and oxide film thicknesses of 0.055–0.118 μm (2.2–4.6 μin.). They noted that mild oxidation of the surfaces had a minimal effect on the surface roughness, and the distribution of asperity heights was nearly Gaussian. Heavily oxidized surfaces, however, exhibited a five-fold increase in roughness over the unoxidized condition and displayed skewed height distributions. The authors further noted that when oxidized surfaces are pressed together, the contact is different from bare metallic surfaces under identical conditions. They stated that the following three ratios influence the contact resistance: 1) the ratio of coating to substrate hardness, 2) the ratio of coating to substrate thermal conductivity, and 3) the ratio of coating thickness to surface roughness. They postulated that if the oxidized coating is much thicker than the roughness, then the resistance increases with increasing coating thickness, whereas if the coating thickness is on the order of or less than the roughness, the resistance will decrease if the coating is much softer than the substrate.

Peterson and Fletcher[8] conducted an experimental investigation of the thermal contact conductance of anodized coatings. Seven anodized samples of 6061-T6 aluminum with coating thicknesses ranging from 60.9 to 163.8 μm (0.0024–0.0065 in.) were tested in contact with a single bare sample. Surface roughness ranged from 0.30 to 5.33 μm (12 to 210 μin.), while asperity slopes varied from 0.08 to 0.25 rad. All surfaces were flat to within approximately 1 μm (39 μin.). Their conclusions indicated that for very smooth, untreated surfaces, slight increases in the roughness cause moderate increases in contact conductance. The overall joint conductance was more sensitive to variations in pressure for the thinner coatings than for the thicker coatings. Using their experimental data, Peterson and Fletcher developed an empirical, dimensionless expression that related the overall joint conductance to the coating thickness, the surface roughness, the interfacial pressure, and the thermophysical properties of the aluminum substrate.

Carbon-Based Coatings

Blanchard et al.[9] conducted a review of the available literature for the thermal conductivity of synthetic single crystal, polycrystalline, and type I and type II natural diamond materials. The values for synthetic diamond were found to depend on the crystal size at low temperatures and on hydrogen impurity and isotopic content at higher temperatures. Impurities that effect chemical vapor deposition (CVD) polycrystalline film thermal conductivity are graphite, amorphous carbon, and carbon hydride, which are present within the film structure. For natural diamond, the thermal conductivity depends primarily on nitrogen impurity concentrations and Umklapp processes at high temperatures, or crystal size and surface conditions at low temperatures.

Hudson[10] conducted thermal resistivity measurements of diamond heat-sink bonds with sputtered titanium and gold films for the temperature range of 1.2–300 K. Epitaxial nickel was introduced to the diamond lattice, and its effect on the thermal resistivity of the bond was also determined. The improvement of the thermal conductivity of the bond with epitaxial nickel was 60% at room temperature. The standard metallic bond with sputtered titanium and gold films was found to be equivalent to 1.2 mm of type IIa diamond at room temperature.

Burgemeister[11] presented thermal resistance data between metal and metallized diamonds and between metallized diamonds bonded together over temperatures from 330 to 450 K. The author's results are analyzed in terms of series resistances due to the change from electron to phonon conduction and due to the nonideal thermal compression bonding technique. Using an infrared detector, the author measured the temperature from a spot at a position x on a black-painted surface as the sample with the various metallized bonds moved underneath the detector, and the interface resistance was derived from the curves.

Caveney et al.[12] conducted indirect thermal resistance measurements for interfaces of diamond (type I) coated with polycrystalline aluminum, nickel (both polycrystalline and epitaxial), and titanium at a temperature of 300 K. The influence of the interfacial resistance became evident when the thermal conductivities of the uncoated and coated (polycrystalline aluminum) diamonds were measured to be 209 ± 25 W/m K and 117 ± 12.5 W/m K, respectively. With an addition of a gold layer on top of the aluminum layer, the conductivity was determined to be 234 ± 25 $W/m^{-1} K^{-1}$.

In order to realize the large range of potential applications of diamond/diamond-like carbon films, it is necessary to be able to 1) deposit these films on a variety of substrates, and 2) achieve heteroepitaxial growth of diamond films. Only limited success has been achieved to date in growing and depositing these films. To overcome the limitations of current processes, an understanding of the nucleation/growth mechanisms must be achieved, and interfacial layers that will enhance growth rates and adhesion to various substrates must be explored.

Ceramics Coatings

Ceramics, in contrast to metals, generally exhibit better structural and thermal characteristics at high temperatures. In general, ceramics are more resistant to creep, oxidation, corrosion, erosion, and wear, as well as being better thermal insulators. New ceramic coating technology is advancing rapidly, new deposition techniques are being developed, and established processes such as evaporation and sputtering are being improved. Examples of relatively new technology are the ion, laser, and sol-gels techniques. The ability to modify and control the microstructure of materials deposited by chemical vapor deposition, the application of high-deposition-rate, rf-magnetron sputtering to ceramics, and the use of reduced pressures in conjunction with plasma spraying are examples of process improvements.

Polymer-Based Coatings

Polymeric coatings, which are designed to provide corrosion protection, must be very tough and durable, and are therefore applied in greater thickness than coatings employed merely for appearance. Polymeric coatings must adhere well to the substrate material, and must not chip or degrade in environmental conditions such as high moisture, salt, or chemicals.

Table 1 Thermophysical properties of selected high-temperature oxides

Material	Name	Density kg/m^3	Melting point, K	Thermal conductivity, W/m K	Thermal expansion coefficient, μm/m K	Elastic modulus, MPa	Bend/fracture strength, MPa	Brinell hardness, MPa
BeO	Beryllia	3,010	2,843	272	9.6	379.21	206.84–344.73	11,760
Al_2O_3	Alumina (corundum)	4,000	2,323	36	7.7	408.85	193.05–344.73	17,640
MgO	Magnesia (periclase)	3,580–3,700	3,098	48.4	10.5	306.12	172.37–337.84	——
$MgAl_2O_4$	Spinel	3,550	2,408	25	8.1	215.11–295.78	130.99	5,684
Fe_3O_4	Magnetite	5,140–5,200	1,863	6	8	——	——	——
SiO_2	Silica (fused)	2,200	1,550–1,700	1.03–1.38	0.55	——	——	——
	(quartz)	2,650	<1,470	9.63	10.7	——	——	4,704
$3Al_2O_3{*}2SiO_2$	Mullite	2,770–3,150	2,083	6.1	4.5	126.86	58.6	5,684
CaO	Calcia (lime)	3,400	2,845	3.5 @ 400 K	0.12	——	——	——
TiO_2	Titania (rutile)	3,840–4,260	2,133	8.4	7.5	——	——	——
$BaTiO_3$	Barium titanate	——	1,890	5.5	6.3	——	——	——
ZrO_2	Zirconia	5,830	2,973	——	8.8	244.07	——	——
	10% CaO stabilized	5,290	2,845–2,973	1.5–2.0	——	148.92	117.21–151.68	14,210
	10% MgO stabilized	5,340	2,973–3,098	——	——	212.36	234.42	14,700
$ZrO_2{*}SiO_2$	Zircon	4,250	1,811	3.8	5.0	——	344.73	——
HaO_2	Hafnia	9,680–10,000	3,173	1.7	3.8	——	——	10,780
$Y2O_3$	Yttria	4,840–5,050	2,683	25	8.2	174.43	261.99–289.58	5,880
$Th2O_3$	Thoria	9,690–10,000	3,573	13.2	9.5	260.62	68.95–103.42	6,272–7,840
UO_2	Urania	10,900	3,153	15	9.4	——	——	——

All property values for 300 K unless otherwise noted.

Acrylics and alkyds are examples of surface-based polymeric coatings which are used extensively for industrial production equipment where corrosion protection is at a premium. Polyurethane enamels are characterized by excellent toughness, durability, and corrosion resistance. Epoxy finishes exhibit better adhesion to metal substrates than most other polymer coatings and are often used as primers under other materials that have good barrier properties but marginal adhesive strength. The general strengths of all the polymeric coatings are that they provide excellent corrosion protection, chemical inertness, and ease of use. The most detrimental characteristic is that they are all poor thermal conductors. The thermal conductivity of the fluorocarbon group can range from 4 W/m K (2.308 Btu/h ft °F) at room temperature to as high as 6 W/m K (3.467 Btu/h ft °F) at 600 K, while other polymeric coatings, such as the previously-mentioned polymers, can be an order of magnitude less.

Impregnated coatings combine the advantages of anodizing (hard-coat) and chemical passivation with a controlled infusion of low-friction polymers and/or dry lubricants. The combined coatings become an integral part of the metal substrate, thus providing increased hardness and surface wear properties. The multistep process incorporates a porous aluminum oxide film grown from the anodization process with submicron particles of fluorocarbon resins to form a continuous plastic/ceramic surface that has greater abrasion resistance than case-hardened steel. Similar impregnation coatings have been developed for steel, stainless steel, copper, magnesium, and titanium, which provide surface improvements such as lubricity, corrosion resistance, and/or wear resistance.

Predictive models have been developed for oxide/anodic coatings and films. These predict an increase in contact resistance due to the decrease in actual contact area and the generally poor thermal conductivity of these films. Models for the prediction of thermal resistance do not exist for the three other categories; thus no conclusive direction in terms of enhancement or reduction in contact conductance can be predicted. However, thermophysical and mechanical properties do exist which can provide insights to enhancement or reduction in contact conductance based on work conducted for metallic and oxide coatings.

Potential Coating Materials

In order to determine which of the nonmetallic materials is most suitable for thermal control applications, a careful review of these materials and their properties was conducted. The review categorizes the nonmetallic materials as oxides, carbon, ceramics, and polymer-based coatings, and each of these categories will be discussed in more detail.

Oxides

Oxides find applications in ceramics, cements, bricks, tiles, glazes, and a host of other uses. A common factor in many of these applications is high temperature. Oxides in their many forms can often withstand temperatures that melt or decompose other classes of materials (e.g., metals, polymers, and composites). Oxides also often exhibit such characteristics as high hardness, and good erosion and corrosion resistance. This review concentrates on refractory or high-temperature oxides, and the thermophysical properties are provided in Table 1.

Alumina

Aluminum oxide, Al_2O_3, or corundum has an NaCl face-centered-cubic (FCC) crystalline structure in which the oxygen anions comprise the lattice, and the aluminum cations occupy two-thirds of the octahedral (six-coordinated) interstitial sites in order to maintain charge balance. Sintered alumina is an electrical insulator and its electrical conductivity is some 20 orders of magnitude smaller than metallic conductors. Alumina has been considered a semiconductor with a very large band gap between the conduction and valence bands.[13–15]

Magnesia

Periclase or MgO also has an NaCl face-centered-cubic crystalline structure in which the oxygen anions again comprise the lattice, and the magnesium cations occupy all the octahedral interstitial sites. Electrical properties of magnesia are very similar to alumina. Its conductivity is also 20 orders of magnitude less than metallic conductors, and it has been considered a large band gap semiconductor.[13–15]

Beryllia

Beryllium oxide, BeO, is of interest to the nuclear industry because of its low neutron-capture cross section and high neutron-moderating capability. Hot-pressed BeO has been used as an internal reflector for nuclear reactors. Apart from reactivity towards water at high temperature, it is one of the most thermodynamically stable oxides up to very high temperatures. It is unique among the refractory oxides in that it has very high electrical insulation characteristics and high thermal conductivity, making it particularly attractive to the electrical and electronics industries, however, its use has been limited because of the health hazards it presents. The electrical conductivity of BeO increases rapidly with increasing metallic impurity content. Its thermal conductivity is sharply reduced by impurities such as CaO, Al_2O_3, and SiO_2.[13-15]

Thoria and Yttria

Thorium oxide, or thoria (ThO_2), is of great potential value to the nuclear industry as a reactor fuel. Its thermal expansion coefficient changes only gradually with temperature due to the absence of any crystallographic transformations up to its melting temperature. It becomes a *p*-type semiconductor at elevated temperatures, and single crystals are of potential interest as optical materials. Yttria, Y_2O_3, also has a fluorite-type structure and exhibits many of the same characteristics as thoria, such as a thermal expansion coefficient that changes gradually with temperature and optical transparency in the pressed, pore-free state.[13-15]

Titania (Rutile) and the Titanates

Titanium oxide, titania, or rutile as the mineral form is called has the composition TiO_2. It possesses a tetragonal crystal structure, and in the reduced state is an *n*-type semiconductor. Iron- or chromium-doped rutile is used as an infrared optical material and for microwave amplification. Titania forms compounds with oxides of the heavier alkaline metals (calcium, barium, and strontium) with the general composition $MTiO_3$ (M meaning a divalent metal). Strontium titanate is also an *n*-type semiconductor. Barium titanate, $BaTiO_3$, is tetragonal at room temperature and undergoes a transition to cubic on heating. Calcium titanate or Perovskite, $CaTiO_3$, is orthorhombic, and its physical properties are similar to those of strontium titanate.[13-15]

Zirconia, Zircon, and Ziconates

The combined properties of chemical inertness and refractoriness make zirconium dioxide or zirconia, ZrO_2, and some of its binary systems particularly useful in heat exchangers, crucibles, and pouring nozzles for molten metals. Zirconia has three well-defined polymorphs, the 1) monoclinic, 2) tetragonal, and 3) cubic structures. Tetragonal zirconia displays *n*-type semiconductivity due to fully ionized oxygen vacancies. Lime- (CaO) stabilized cubic zirconia is far more stable than magnesia-stabilized zirconia and possesses a high electrical conductivity at temperatures greater than 1000°C. Hence, it is used to make furnace elements and solid state electrolytes in fuel cells. The thermal conductivity of calcia- (lime) stabilized cubic zirconia is low and nearly temperature independent. This behavior is not typical of refractory oxides and resembles the conductivity of a glass. It exhibits high thermal shock resistance. Stabilizers mixed with certain rare earths of yttrium result in increased thermal conductivity and thermal shock resistance.[13-15]

Hafnia

Hafnium oxide, HfO_2, is one of the most stable refractory compounds known, with a melting point of 2900°C. Of the oxides, only thoria has a substantially higher melting point. All chemical properties of hafnium compounds are remarkably similar to those of zirconium. However, differences in the physical properties of hafnia and zirconia are great.[13-15]

Carbon

In order to evaluate carbon as a coating material for thermal control, it is appropriate to consider the various forms of carbon and their particular attributes. These carbon polymorphs are single crystal diamond, polycrystalline diamond films, and diamond-like films.

Single Crystal Diamond Films

Due to its excellent thermal and electrical properties, diamond appears to be one of the most promising materials for meeting the thermal and electrical requirements of future advanced electronic packages. A group of crystals whose thermal conductivity at room temperature exceeds 100 W/m K are called adamantine compounds. These compounds, such as diamond, silicon carbide, silicon, beryllium oxide, aluminum nitride, cubic BN, and BP, all possess atoms with a tetrahedral coordination, and as such should have thermal conductivities at 300 K of greater than 100 W/m K. The plot of thermal conductivity of these compounds as a function of temperature is presented in Fig. 1 for single crystal material. Beryllium oxide is not included because it is polycrystalline. The plot clearly shows that diamond exhibits the highest thermal conductivity from room temperature to 30 K.

The thermal conductivity of diamond as a function of temperature for the maximum thermal conductivity values measured is shown graphically in Fig. 2. Data for both natural and synthetic single crystals as well as data for polycrystalline films are shown. The data explicitly show that type IIa has the highest *k* value of the four types, and type Ia the lowest. This can be attributed to the amount of nitrogen impurity present either as dispersed or clustered atoms. Depending on the deposition technique, polycrystalline films can have thermal conductivity values ranging from 450 to 1700 W/m K, which approaches that of diamond type IIa (2000 W/m K).

Polycrystalline Diamond Films

Many different processes and deposition techniques have been developed for the deposition of thin diamond films. The

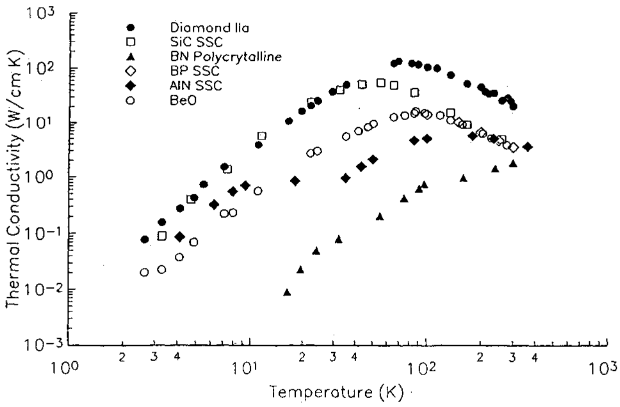

Fig. 1 Thermal conductivity of the adamantine compounds.

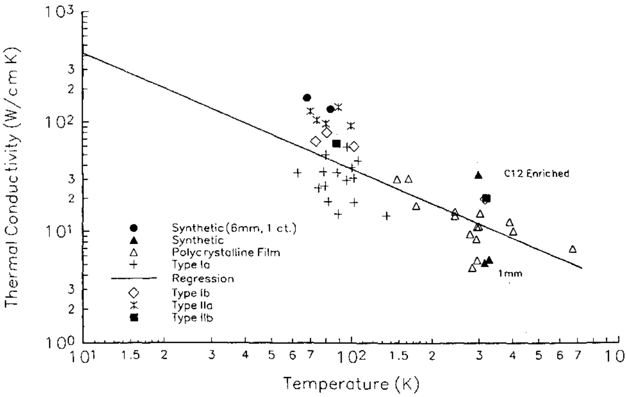

Fig. 2 Thermal conductivity (maximum values).

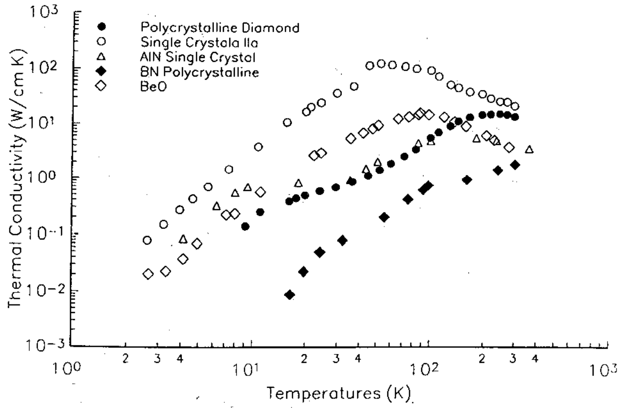

Fig. 3 Thermal conductivity of polycrystalline diamond vs adamantine compounds.

films grown from these processes are generally polycrystalline in form, but differ in growth rates, crystallite size, and the graphite content incorporated within the film structure. Whereas the cost of natural diamond has limited their use to applications requiring very small surface areas, such as laser diodes, diamond films grown by chemical vapor deposition can offer both low cost and large surface area coverage. The result is that free-standing diamond films can be used in high-power electronic packages as a heat sink or thermal spreader material.

The adhesive strength between any substrate material and the diamond film itself must be high enough to withstand stresses generated by the differences in coefficient of thermal expansion during cooling and then by rapid thermal cycling. This can be accomplished by the use of interfacial layers between the substrate material and the diamond film. In the case of copper, an interfacial layer of epitaxial nickel combined with amorphous silicon or silicon nitride can provide improved film adhesion. For aluminum alloys the metallic substrates must be joined with a metallized free-standing diamond film since deposition temperatures of 750–900°C would melt or change the physical characteristics of the alloy.

Both natural and synthetic single crystal diamonds have electrical resistivities from 10^8 to 10^{14} Ω-m. CVD polycrystalline films have shown resistivities approaching values as high as 10^{13} Ω-m. Polycrystalline diamond films have also been shown to have dielectric constants approaching that of natural diamond (5.7), and dielectric strengths of 10×10^{14} V/m. With these unique physical properties, diamond films are ideal candidates for heat-sink or heat-spreader applications for electronic packages.

Two other physical properties worthy of mention are the physical hardness (i.e., polycrystalline diamond Vicker's hardness $\approx$ 10,000 kgf/mm^2; natural diamond: Vicker's hardness $\approx$ 7000–10,000 kgf/mm^2), and inertness to any known chemical. Polycrystalline diamond films also possess a coefficient of friction equivalent to Teflon® (i.e., 0.08–0.2) which makes them ideal as wear-resistance coatings, especially for card rail assemblies.

Figure 3 illustrates the comparison between the thermal conductivities of polycrystalline diamond films grown by microwave plasma chemical vapor deposition (MPCVD) and the adamantine compounds. The diamond film conductivity approaches that of the single crystal diamond (type IIa), and is much higher than the conductivity of the other compounds at room temperature.

Diamond-Like Films

These films are often produced from a plasma of ionized hydrocarbon species and, depending on the method of preparation, can contain substantial amounts of hydrogen (up to 30% atomic). The greatest difference between diamond and diamond-like films is the deposition temperature. The range of temperatures for diamond-like films is 150°–300°C, while for diamond films it ranges from 700 to 900°C. The relatively low range of deposition temperatures required for diamond-like films increases the number of potential substrate materials on which the films can be deposited, and reduces thermal stresses at the interface.

Savvides and Window[16] have produced thin films of amorphous carbon (a-C) containing no hydrogen, yet still possessing diamond-like properties. By carefully controlling sputtering power and keeping other deposition parameters fixed, they could reproducibly grow an a-C film with diamond-like properties. Vicker's hardness ranged from 2400 kgf/mm^2 (comparable to sapphire) for coatings deposited at low power, $\leq$20 W, to 1350 kgf/mm^2 for those deposited using a power level of 300 W.

Hydrogenated diamond-like films are characterized by extreme hardness, measured to be in the range of 3000–9000 kgf/mm^2, and a generally low friction coefficient, between 0.01 and 0.28. These properties make these films useful as a wear-resistant coating even at very low thicknesses ($\sim$2–3 μm). Hydrogenated diamond like carbon (DLC) films are also characterized by very high electrical resistivity, in the range of 10^3–10^{13} Ω-m, depending on the deposition conditions. The films are expected to have a relatively high thermal conductivity due to its diamond-like properties. The exact value has not been measured since the DLC films can be deposited only in small thicknesses because of high internal stress.

Due to the relative softness of both aluminum and copper alloys in comparison to the diamond-like film, a rigidizing layer a few micrometers thick must be deposited between the DLC film and the metallic substrates to reduce eventual cracking of the hard layer under possibly large bending strains. A Ni layer is used as a barrier layer to prevent the diffusion of the a-Si:H rigidizing layer into the copper substrate, in addition to providing improved adhesion of the overall structure to the copper or aluminum alloy. Other rigidizing layers such as TiN or silicon nitride can be substituted for a-Si:H. A comparison of physical properties of hydrogenated DLC films with natural diamond and graphite was conducted by Roberton,[17] which is presented in Table 2.

Ceramics

Ceramic coatings can be applied by techniques which affect their physical and thermal properties. These processes include plasma/flame spraying and CVD refractory deposition. A subcategory of plasma/flame coatings are called thermal barrier coatings (TBC) which are used primarily for thermal protection, wear resistance, and thermal insulation.

Plasma/Flame Spray Coatings

A plasma is a gaseous cloud composed of free electrons, positive ions, neutral atoms, and molecules. The plasma is formed at temperatures above 20,000 K, at which there is sufficient energy imparted to a gas to cause ionization. This high-temperature plasma, when caused to flow as a jet, provides an ideal means for melting and propelling particles of materials onto the surface of a substrate. It is this phenomenon that enables plasma-spraying equipment to apply numerous materials as a coating on various substrates. Flame-sprayed coatings have found wide acceptance as both protective and decorative coatings. Plasma and flame spraying are distinguished by the fact that the feed materials for plasma spraying are powders, while prefabricated rods of the coating material are used for flame spraying.

Ceramic flame-sprayed coatings include the oxides, carbides, borides, nitrides, and silicides, as well as a number of glass compositions. These ceramic coatings have been used for thermal insulation, electrical insulation, and erosion and corrosion resistance. A compilation of reported properties for plasma-sprayed ceramic coatings is presented in Table 3.[18–21]

Table 2 Physical properties of various forms of carbon[17]

Material	Density, kg/m^3	Electrical conductivity, Ω-m^{-1}	HV,[a] kgf/mm^2	E_{opt}, eV
Diamond	3515	10^{-16}	10^4	5.5
Graphite	2267	2.5×10^6	——	−0.04
Glassy carbon	1300–1550	10^4–10^5	800–1200	10^{-2}
Evaporated a-C	2000	10^5	20–50	2.00
Ion-beam a-C	1800–2700	10	——	1.8–2.7
a-C:H	1400–1800	10^{-5}–10^{-14}	1250–6000	1.4–1.8

[a] Vicker's hardness.

Table 3 Thermophysical properties of flame-sprayed coatings

Material	Density, % of bulk material	Melting point, K	Thermal expansion, ($C^{-1} \times 10^{-6}$)	Thermal conductivity, W/m K	Specific heat, kJ/kg K	Dielectric constant	Hardness, MPa
AlO_3	85–91	1,921	7.14–12.50	20.77–34.61	1.256	10	13,720–19,600
$BaTiO_3$	80–90	——	——	——	——	23.5–500	——
Be	85–90	——	——	——	——	——	——
ZrB_2	93	——	——	——	——	——	9,800
ZrC	——	——	——	——	——	——	7,840
CrC	96–97	——	——	——	——	——	——
HfC	81–87	——	——	——	——	——	3,920–7,840
TaC	——	——	——	——	——	——	2,940–9,800
WC	90	——	——	——	——	——	3,920
CeO_2	92	——	——	——	——	——	——
Cr_2O_3	90–95	1,921	8.93	31.15	0.837	——	11,760
HfO_2	87	——	——	——	——	——	2,450–3,038
MgO	85–90	2,199	8.03	31.15	1.046	——	——
Mo	88–93	2,899	6.25	——	——	——	3,920–4,900
NiAl	85–95	——	——	——	——	——	1,519
TiN	——	——	——	——	——	——	7,654–10,731
ZrN	——	——	——	——	——	——	6,105–10,976
TiO_2	70–85	2,033	5.71–8.75	25.96	——	——	14,700
W	80–93	——	4.82	——	——	——	1,636.6
ZrO_2	85–95	2,755	5.36–12.50	6.9–13.84	0.712	35	5,880–7,840
$ZrSiO_4$	85–90	1,921	7.14	25.96	0.628	15	9,800

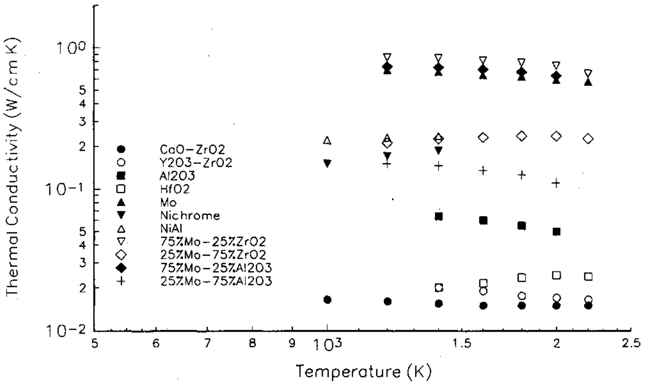

Fig. 4 Plasma sprayed coatings.

The most frequently used oxide coatings are alumina and zirconia. Both coatings are used primarily for thermal and electrical resistance, but the higher melting point of zirconium oxide extends its range for thermal applications. Carbide coatings are used for wear resistance and thermal resistance in reducing atmospheres. Cobalt, nickel-chromium, and other metals are added in small percentages as fluxes and to improve bonding characteristics.

The key attributes of flame-spray coatings are high melting temperatures, good thermal and electrical insulation, good erosion and corrosion resistance, but low thermal conductivity when compared to bulk conductivity. Poor thermal conductivity is directly related to the porous nature of the coating. Thermal contact conductance data for the plasma-sprayed coatings presented in Table 3 were not found, but based on the low thermal conductivity data at room temperature, the predicted contact conductance will also be low.

Wilkes and Lagedrost[18] conducted thermal conductivity vs temperature measurements of several plasma-sprayed coatings (post high-temperature heat treatment), as presented in Fig. 4. The researchers concluded that the thermal conductivity increases were a function of heat treatment temperatures and times, with heat treatment temperature the major variable.

Thermal Barrier Coatings

One of the important applications of ceramics is in coatings applied to metals for thermal protection, wear resistance, and thermal insulation. Thermal barrier coatings (TBC) are used for thermal insulation and protection of metallic substrates. These coatings are characterized by very low thermal conductivities (generally <2 W/m K for temperatures up to 1500 K), high porosity, and the ability to withstand high temperatures (>2000 K).

Brandt et al.[19] measured the thermophysical properties of three yttria-stabilized zirconia barrier coatings in the temperature range of 300–1500 K. They also conducted thermal conductivity measurements on nickel-aluminum and nickel-chromium (cobalt, aluminum, yttrium) plasma-sprayed coatings. Figure 5 illustrates graphically the thermal conductivity vs temperature of these metallic coatings, which are also considered thermal barrier coatings due to their low thermal conductivity. The data explicitly shows that coatings sprayed under vacuum conditions have higher thermal conductivities (twice that of air-sprayed coatings), principally due to their lower porosity and lower oxide contents.

CVD Refractory Coatings

Refractory coatings, such as TiC, TiN, SiC, Cr_7C_3, Fe_xB, and Al_2O_3, can be used for wear-resistant and corrosion-protective applications for different environmental conditions.

Table 4 Properties of various polymers used as coatings

	Physical		Mechanical		Thermal		Electrical		
								Dielec. con.,	
Material	Specific gr.	Water absorp., % in 24 h	Hardness, Rockwell	Tensile st., MPa	Therm. cond., W/m-K	Thermal expansion $(\mathrm{C})^{-1} \times 10^{-5}$	Dielec. st., MV/m	1 kHz	1 MHz
Acrylic									
Standard	1.19	0.3	M95	72.4	——	3.6	19.6	3.3	2.3
High impact	1.15–1.17	0.3	M68	37.2–48.3	——	3.8	15.1–17.7	3.9	2.5–3.0
Alkyd (filler)									
Mineral	1.60–2.30	0.05–0.05	E98	20.7–48.3	0.51–1.05	2–5	13.8–17.7	5.5–6.0	——
Glass	2.0–2.3	0.03–0.5	E95	27.6–62.0	0.63–1.05	1.5–3.3	9.8–20.9	——	——
Allyl									
Polyester	1.39–1.42	0.2	M108	34.5	——	——	15.7	0.008	——
Long glass	1.70–1.90	0.05–0.2	M105–110	62.0	0.59–0.67	2.0–3.0	15.1	0.004–0.006	——
Short glass	1.60–1.80	0.05–0.2	M105–110	48.3	0.59–0.63	2.0–3.0	15.7	0.006	——
Epoxy (molding)									
Glass-fiber	1.6–2.0	0.05–0.20	100–110	68.7–137.9	0.17–0.42	1.1–3.5	11.8–15.7	3.5–5.0	——
Mineral filler	1.6–2.0	0.04	100–110	34.5–68.9	0.17–1.25	2.0–5.0	11.8–15.7	3.5–5.0	——
Fluoroplastics									
PTFE (Teflon)	2.13–2.24	<0.01	D50–65	23.1	2.90	5.5–8.4	19.6–23.6	2.1	——
FEP	2.12–2.17	<0.01	D55	20.7	2.42	4.6–5.8	19.6–23.6	2.1	——
PFA	2.12–2.17	0.03	D60	27.6	3.11	6.7	19.6–23.6	2.1	——
PVDF	1.75–1.78	0.04	D80	35.8–51.0	1.2–1.55	8.0–8.5	10.2	7.5	——

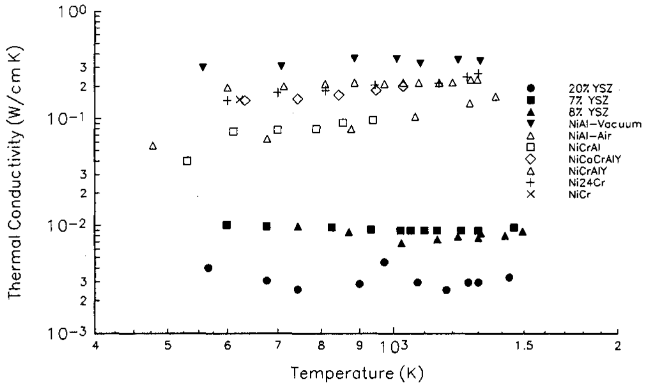

Fig. 5 Thermal conductivity—thermal barrier coatings.

CVD is an important technique for deposition of these refractory compounds since the use of low pressures (<1 atm) improves the coating homogeneity and the interfacial adhesion to the base substrates. During high temperatures (>500°C), the coating material can react with the substrate material to form solid solutions (by diffusion), intermetallic compounds, or coatings of carbides, nitrides, or carbonitrides (when deposition is carried out in the presence of hydrocarbons or nitrogen-containing compounds). These coatings are very hard; thus they can only deform elastically and cannot withstand mechanical overloading without a risk of cracking. The coefficients of thermal expansion of the refractory coatings differ widely among each other, but also differ widely with many base substrate materials, as can be seen in Table 4.

One of the beneficial effects of the high temperatures in CVD is that the bond strength between the coating and the substrate material is very high. Both the coating and the material form transition zones by interdiffusion. These zones can be a few micrometers thick or as thin as a few atomic layers, depending on the material combination. Cemented carbide steels, when coated with TiN, can form intermediate layers of TiC and titanium carbonitride (Ti-C, N) which greatly enhance the bond strength between coating and substrate.

Refractory coatings deposited by a CVD method have found widespread acceptance for the protection of bearings, forming tools, and cutting inserts. Their mechanical properties and chemical stability are also useful in the microelectronic industry, where protective coatings are essential for electronic packaging of high-powered chips.

Polymer Base Coatings

Polymeric coatings are designed to provide corrosion protection against many environmental conditions. They can be applied as surface coatings, with acrylic and alkyd polymers, or they can be impregnated into the top surface of metallic substrates through a controlled infusion of size-controlled resins in porous oxides. A summary of the thermophysical and mechanical properties of polymer-based materials is provided in Table 4.[22]

Surface Coatings

Polymeric coatings such as acrylics and alkyds, epoxies, and fluorocarbons have found extensive use because of their excellent corrosion protection and their ease of application. Acrylics have good dimensional and structural stability as well as good thermal and optical properties. Properties such as dimensional stability and transparency are unaffected by long exposure to the elements, salt spray, or corrosive atmospheres.

Alkyds are compounds that are based on unsaturated polyester resins which are combined with monomers, reinforcements, and fillers. Low moisture absorption, dimensional stability, and good electrical insulation properties are characteristics of most alkyd compounds. Alkyds with mineral fillers have high moisture resistance and can withstand the temperatures of vapor-phase soldering, which has led to wide spread acceptance for electronic components. They retain their electrical and mechanical properties up to 177°C (350°F) for long duration, and up to 232°C (450°F) for short periods.

Epoxies are polymers which have been cured to form thermoset resins by two methods: 1) homopolymerization of epoxy groups with themselves, or 2) curing agents such as anhydrides, amines, and novolacs. Epoxies have good electrical and thermal insulating properties as well as good chemical resistance. Glass-fabric-reinforced epoxy polymers are used in the electronic industry for printed-circuit boards. Encapsulation of electrical and electronic components ranging from semiconductor chips to large motors are other applications of epoxy polymers.

Fluoroplastics are polymers in which all or some of the hydrogen is replaced by fluorine. They have good heat and chemical resistance, which makes them good candidates for coatings of metals and anodized aluminum. All fluoroplastics have electrical insulation properties that remain stable over a wide range of frequency and environmental conditions. For electronic applications, their low dielectric constant and electrical loss (2.1 and 0.001, respectively) over the range of 60 to 10^9 Hz make them ideal materials for insulation purposes.

Impregnated Coatings

Combination or synergistic coatings combine the advantages of anodization or case hardening with the controlled infusion of low-friction polymers (fluoroplastics) or dry lubricants to improve the tribological properties of the base metal. For aluminum, the anodization process forms a porous oxide by which size-controlled dispersions of polytetrafluoroethylene resins are diffused into the oxide at elevated temperatures [315°C (600°F)]. The process essentially replaces the water molecules in the aluminum oxide surface with low-friction polymeric materials. The resultant surface provides permanent dry lubricity, added wear and corrosion resistance, and high chemical and dielectric strength. The thermal conductivity of the polymeric material (Teflon) is approximately 3 W/m K (1.73 Btu/h ft°F).

Similar impregnation coatings have been developed for ferrous metals, copper alloys, and titanium. These synergistic coatings require a hard layer of nickel to be deposited onto chemically clean surfaces. Micro pores which are developed during deposition are enlarged through chemical etching, and then the top surface layer is impregnated with polymeric particles. High temperature posttreatment insures integration of the polymers throughout the top layer. The resultant hardness is greater than hard chrome plating; the wear rates are reduced from 134.4 (electroless nickel—no heat treatment) to 3.0 mg; and corrosion resistance is improved from 100 h (salt spray test) to 1200 h.

The use of synergistic coatings can be employed for ceramic coatings (alumina, chrome oxide, and tungsten carbide), combinations of metals, titanium, and magnesium alloys. Since these coatings are proprietary, the exact thermophysical and mechanical properties of synergistic coatings are not well known.

Conclusions and Recommendations

A survey of the thermophysical and tribological properties of four groups of nonmetallic materials was undertaken to evaluate the performance of these coating materials in terms of their application to SEM. The four groups consist of oxide materials, carbon-base coatings with stable tetrahedral bonding, ceramics (both as a thermal barrier and thermal enhancer), and polymer-based (surface and impregnated) coatings. Potential coating materials from these groups will be identified for further investigation of their thermal contact conductance based on their physical properties.

Within the oxide coating group, beryllia (BeO) is the choice as a suitable coating for thermal control applications due to its high thermal conductivity in comparison to other oxide coatings. The thermal conductivity of beryllia is a factor of 8 greater than alumina and a factor of 6 greater than magnesia. Other oxide coatings such as silica (SiO_2), titania (TiO_2), zirconia (ZrO_2), and barium titanate ($BaTiO_3$) have thermal conductivity values less than 1 W/m K. However, beryllia's high hardness (1200 kg/mm^2) will be detrimental to the contact conductance in microelectronic applications unless the oxide film is contacting a softer coating material such as silver. Beryllia's other shortcoming is that the manufacturing process is extremely hazardous since beryllia is toxic, and safety precautions must be taken.

While oxide films can easily be grown on many different metallic substrates by chemical conversion processes, they must remain relatively thin (less than the surface roughness), and oxide hardness must be less than the substrate for any beneficial enhancement to the contact conductance. Anodic coatings processed at room temperature or higher would result in softer coatings which may enhance the contact conductance. Therefore, anodic coatings grown at room temperatures or higher is a recommendation from this group.

Carbon-based coatings such as polycrystalline diamond and diamond-like films offer excellent thermophysical and tribological properties which make them an attractive alternative to present coatings. Since both types of films are difficult to deposit directly onto aluminum or copper, interfacial layers which provide adhesion and stability must be introduced. Such a rigidizing layer exists for diamond-like films, but one must be developed for polycrystalline diamond films. Deposition temperatures of polycrystalline diamond films will also limit these films to metals that can withstand high temperatures (700–900°C) without loss of intrinsic properties. This technical obstacle may limit the application of these films for aluminum and its alloys, but may not affect copper and its alloys. This obstacle may be overcome by the use of a dual-ion beam technique which has deposition temperatures below 600°C (1112°F), but this will need further process development. The use of free-standing films which are soldered to the metal substrate may also be a solution. Thus, both polycrystalline diamond film and diamond-like film should be considered for microelectronic applications.

Impregnation coatings (synergistic coatings) combine the properties of two or more materials (i.e., polymer resins, oxides, ceramics, and nickel) to provide a surface with permanent dry lubricity, added wear and corrosion resistance, and high chemical inertness. Salt spray testing has shown a factor of 12 increase in corrosion resistance when compared to nickel-plated surfaces. Both the coefficient of friction and wear resistance have been improved. These synergistic coatings can be easily applied to both aluminum and copper as well as their alloys. These coatings could be substituted for present coatings to provide greater corrosion protection and possibly better thermal control characteristics for selected applications.

Ceramics generally exhibit good structural and thermal capabilities at high temperatures. They are more resistant to oxidation, corrosion, erosion, and wear than most metals. Through the use of chemical vapor deposition, oxidation-resistant coatings can be applied to carbon, metal matrix, and carbon-carbon composites to form a uniform coating on complex shapes. Such coatings as titanium nitride (TiN), titanium carbide (TiC), and silicon carbide (SiC) have shown good thermal and mechanical properties. These coatings can be applied to complex shapes and have wear rates less than 5×10^{-6} mm^3/m for high relative humidity. These coatings could be alternatives for the nickel plating and anodization presently used for the SEM. Aluminum nitride also exhibits good mechanical, electrical, and thermal properties which makes it an attractive replacement for anodization on aluminum, without any loss to chemical and environmental stability. Unfortunately, ceramic coatings are extremely hard and thus must be used in conjunction with a soft coating. These coatings are not recommended for most thermal enhancement applications, but are suitable for thermal barrier applications.

Polymeric coatings have excellent properties for environmental protection of various metals and nonmetallic materials. They provide good dimensional and structural stability along with good electrical insulation properties. These coatings would provide ideal protection for microelectronic applications for corrosion purposes, but the extremely low thermal conductivities would be detrimental to the thermal contact conductance between components. These materials would be ideal if we wanted to increase the contact resistance, increase electrical insulation, decrease the static and dynamic friction coefficients, and provide a thermally stable coating.

Acknowledgments

Support of this investigation was provided by the Office of Naval Technology (ONT), Arlington, Virginia, and by NSWC, Crane, Indiana, through Contract N00164-91-C-0043.

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