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Au/(Ti–W) and Au/Cr metallization of chemically vapor-deposited diamond substrates for multichip module applications

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Abstract

Since diamond obtained by chemical vapor deposition (CVD) has an extremely high thermal conductivity, it holds great promise in solving thermal management problems in high performance multichip modules (MCMs). Consequently, there is a need to develop a reliable metallization system for CVD diamond. Refractory metals such as Ti, Mo, Ta and W are known to form adhering carbide layers at high temperatures. Also, transition metals such as Cr, Ni and Ni–Cr are widely used in other MCM technologies involving Si, AlN, SiC and alumina substrates. In the work reported here, adherent Au/Cr and Au/(Ti–W) metallization systems were produced at low temperatures using d.c. magnetron sputtering and electron beam evaporation techniques. Adhesion at low temperature is essential since CVD diamond could lose its thermal and electrical properties at high temperatures. Furthermore, interaction between metal layers may cause an increase in conductor trace resistivity and delamination. Adhesion was measured using a Sebastian V-A thin film stud pull tester. The deposition parameters were optimized to give maximum adhesion using a statistical design software package, ECHIP. In the case of the sputtered metallization, pre-sputter cleaning of diamond surface improved adhesion significantly. Values above 9 klbf in^{-2} were obtained in the case of Au/(Ti–W) and 11.8 klbf in^{-2} in the case of Au/Cr. Post-deposition annealing was performed in nitrogen ambient to investigate the effect of post-metallization processing on adhesion and also to test for any possible interaction between the metals at high temperatures. Annealing temperatures were limited to 450 °C since MCM substrates are seldom exposed to temperatures higher than these. Energy-dispersive spectroscopy (EDS) analysis indicated outdiffusion of W through Au at 400 °C. No interdiffusion was observed in the case of Au/Cr as per optical microscopy and EDS analysis. Auger electron spectroscopy results indicate interaction between the metals in both Au/(Ti–W) and Au/Cr metallizations at 450 °C.

Keywords: Chemical vapour deposition; Diamond; Gold; Metallization

1. Introduction

Multichip packaging technology has received widespread attention in the electronics industry. The use of multichip modules (MCMs) promises to increase packaging density and system performance beyond what is otherwise possible through the use of very-large-scale integration and surface mount technology [1]. As in the case of most advanced technologies, the drive towards high performance MCMs has given rise to a number of engineering challenges. In advanced MCMs where high speed, high-power chips are mounted shoulder to shoulder on large circuit boards, heat spreading and removal become major issues. Diamond has the highest known thermal conductivity and at the same time is an electrical insulator. It holds great promise in solving thermal management problems in MCMs. The use of diamond substrates may also make the use of three-dimensional MCMs possible.

1.1. Diamond as a substrate

Substrate materials are chosen on the basis of dielectric strength, dielectric constant, dissipation factor, thermal conductivity, thermal expansion and surface finish. Substrate material choices have essentially been limited to silicon, aluminum oxide and to a much lesser extent AlN, SiC and glass–ceramics. Today, AlN substrates and packages are serious contenders in many new thermal packaging designs. However, power dissipation in some next-generation equipment will require materials capable of removing heat more efficiently than AlN or even copper.

Recently, there has been considerable progress in the preparation of diamond and diamond-like films and even of free-standing diamond substrates. High purity diamond exhibits thermal conductivities five times higher than copper and is being developed as a sub-

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strate or heat sink for high power radar, microwave and super computer applications [2].

Diamond has an additional advantage. Its thermal expansion coefficient is similar to that of silicon and silicon dioxide. Other attractive properties of diamond as a substrate include good mechanical strength, low dielectric constant, excellent dielectric properties, non-toxicity and stability under working conditions. It can also withstand high thermal shock [3].

1.2. Metallization systems

The desirable characteristics of a metallization system are good adhesion to the substrate, low stress, good electrical conductivity and minimal reactions at subsequent processing temperatures (up to 400 °C) [4]. Gold was chosen as the metal for the conductive layer for its superior electrical conductivity and ease of deposition. Gold protects the surface from environmental attack and helps to ensure bondability. It has good solderability and is an extremely inert metal which protects it from oxidation. However, as gold is a noble metal, is expected to have poor adhesion to diamond, which itself is chemically inert.

Two classes of metals have been reported to form carbides with diamond at high temperatures [5]. These are refractory metals such as Ti, W and Mo and transition metals such as Cr, Ni and Fe. Roser [6] reported that refractory metals from carbide precipitates at the metal–diamond interface. These carbide precipitates were reported to result in stable, adhering, ohmic contact to diamond. Moazed *et al.* [7] and Venkatesan and Das [8] also reported carbide formation for Mo/Ni and Ti metallizations at 950 °C and 850 °C respectively. However, temperatures as low as 580 °C were reported by Gildenblat *et al.* [9] for carbide formation with Au/Ti on diamond films obtained by chemical vapor deposition (CVD) [9]. Cr has been used extensively in many MCM technologies as adhesion promoter and diffusion barrier metal. In this study, we investigated Au/(Ti–W) and Au/Cr metallizations for potential use as high density interconnects on diamond-based MCMs.

Since it is expected that CVD diamond undergoes some change in its properties at elevated temperatures, and since interdiffusion of metals may cause increase in the resistivity of Au conductor traces and even delamination, it was proposed to study the adhesion properties of these metals at low deposition and annealing temperatures. In the case of sputtered metallization, improvement in adhesin was saught by activating the surface carbon atoms of diamond using a sputter-etching treatment.

2. Experimental details

A Perkin–Elmer Randex 2400 diode sputtering system was modified to do d.c. magnetron sputtering and a CVC electron beam evaporater was used to deposit films by the evaporation technique. In order to investigate several metallization systems to achieve adherent conducting films on diamond substrates (that would meet stringent quality control specifications for MCM applications), the effects of various deposition variables on adhesion were studied. Since sputtering and evaporation involve many control variables such as deposition rate, power, pressure, substrate etch, deposition time and sputter etch time, a one-variable-at-a-time approach to optimize adhesion becomes prohibitive.

Thus a statistical design that minimizes the number of experiments to be performed was followed. In this approach, any interaction between the control variables is easily detected. Furthermore, regression models can be used to give an optimum set of control variables for the desired response values. Of the several software packages available, the response surface methodology supported by ECHIP was used in this study.

The free-standing diamond substrates used for this work were supplied by Norton Diamond Films, Northboro, MA, and were grown using a magnetically enhanced d.c. arc jet technique. This system gives large-area (up to 15 cm diameter), high quality, free-standing substrates at very high deposition rates. The substrates used for this work had a surface roughness of less than 1 μm (after polishing) and a dielectric constant of 5.57.

The diamond substrates were laser cut to either 9 mm × 6 mm or 5 mm × 5 mm in size. These samples were lapped–polished and plasma etched to remove graphite from their surfaces. They were cleaned in trichloroethylene, acetone and methoanol solutions (in that order) in an ultrasonic cleaner just before metallization. In that case of sputtering, the films were deposited at a chamber pressure of 10 mT (base pressure, (2–4) × 10^{-6} T) in argon to a total thickness of 5000 Å (2000 Å of Ti–W or Cr and 3000 Å of Au). These films were furnace annealed in a nitrogen ambient for 30 min.

Testing for adhesion was performed using a Sebastian V-A thin film adhesion tester. Epoxy-coated aluminum studs, 2.7 mm in diameter, were attached to the samples by curing at 150 °C for 1 h. Analytical techniques such as sheet resistance measurements, optical microscopy, energy-dispersive spectroscopy (EDS) and Auger electron spectroscopy (AES) were used to study the extent of interdiffusion between the films.

3. Results and discussion

3.1. Au/(Ti–W) metallization system

A tabulation of adhesion values obtained for the 17 experiments as suggested by ECHIP is shown in Table 1. The response surfaces plotted using ECHIP are shown in

Table 1
Adhesion values of Au/(Ti–W) diamond samples

	d.c. power (W)	Sputter etch power (W)	Sputter etch time (min)	Adhesion (klbf in^{-2})
1	150	15	50	9.09
2	50	10	150	0.73
3	50	15	50	7.93
4	150	5	50	4.51
5	150	15	150	9.09
6	100	15	100	0.941
7	100	10	50	3.61
8	150	10	100	8.54
9	50	5	50	4.71
10	100	5	150	6.47
11	100	15	150	9.09
12	50	15	100	9.09
13	50	5	100	9.09
14	150	10	150	3.21
15	50	10	50	4.23
1	150	15	50	8.39
2	50	10	150	1.029

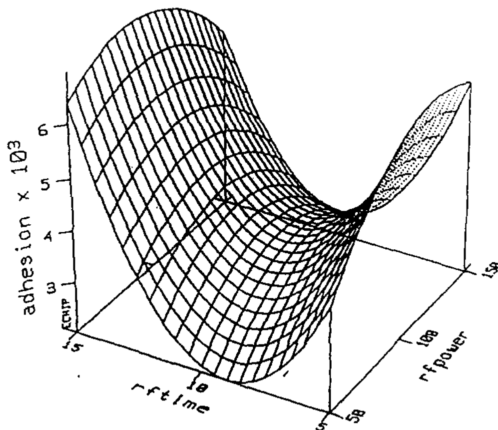

Fig. 1. Response surfaces for Au/(Ti–W)/diamond samples.

Fig. 1. As the table shows, adhesion values up to 9 klbf in^{-2} were obtained. The pull test was not performed at higher values because the substrates tended to break above this stress value. Experiments without a substrate sputter etch gave adhesion values around 0.2 klbf in^{-2} as opposed to values as high as 9 klbf in^{-2} for samples exposed to a sputter etch prior to metal deposition.

The response surfaces indicate that a sputter etch power of 100 W gives maximum adhesion. A sputter etch power of 150 W also gives good adhesion if the etch time is 5 or 15 min. An etch time of 10 min gives minimum adhesion. A possible explanation for this is that etching for a short time activates the surface sufficiently for good adhesion, but continued etching may result in the formation of a graphitic layer that is not a good adhering layer. Further etching (15 min) may then remove the graphitic layer and expose the diamond surface for the deposition of metal layers.

No change was observed in the adhesion values when the samples were annealed at 150 and 300 °C. However, when they were annealed at 450 °C, samples that initially gave an adhesion value of 9 klbf in^{-2} (good adhering films) and 1.8 klbf $^{-2}$ (poorly adhering films) degraded to 5.75 klbf in^{-2} and 0.3 klbf in^{-2} respectively. The surface was observed under an optical microscope and was seen to turn slightly bluish green along the grain boundaries (Fig. 2(a)). The adhesion degradation can be attributed to the outdiffusion of Ti–W to the surface of gold where it oxidized owing to the presence of trace amounts of oxygen and/or moisture in the purge gas. The presence of oxygen in the annealing ambient may have exacerbated this outdiffusion owing to what is known as "ambient effect" [10]. Similar studies were performed using silicon substrates that also showed a significant number of defects appearing on the surface at 450 °C (Fig. 2(b)).

The energy-dispersive spectra of samples annealed at 150 and 300 °C showed only the Mα characteristic peak of Au at 2.14 keV. The Ti Kα and W Mα peaks did not appear, but, for the sample annealed at 450 °C, the W Mα peak appeared at 1.79 keV. These results strongly support the explanation given for the discoloration of Au at 450 °C.

The compositional Auger depth profiles of the samples are shown in Fig. 3. No changes were observed for the 150 and 300 °C sample, but, at 450 °C, very interesting observations can be made. There are two regions where the W concentration exhibits a maximum. A scanning electron photomicrograph taken after the depth profile also confirmed this observation (see inset of Fig. 3). It can be seen that there is complete interdiffusion between Ti–W and Au. Ti and W outdiffuse through the Au layer first. About 60 at.% W and 15 at.% Ti were present at this point. The Au concentration was only 25 at.% in this region, but, Au outdiffused through Ti and W, resulting in 80 at.% Au at the surface with only 10 at.% W and 5 at.% Ti. Clearly, this interdiffusion can only be attributed to grain boundary diffusion since the bulk solubility of either metal (Ti–W or Au) in the other is very small. The metal layers are therefore not stable at this temperature. It can also be seen that the slope of the C profile decreases considerably in the 450 °C sample compared with the 300 °C sample. This means that C atoms are slowly diffusing into the Ti and W regions, possibly forming TiC and WC.

3.2. *Sputtered Au/Cr metallization system*

The Au/Cr/diamond samples deposited using the sputtering system gave adhesion values above 3 klbf in^{-2}. Adhesion testing was stopped at this point be-

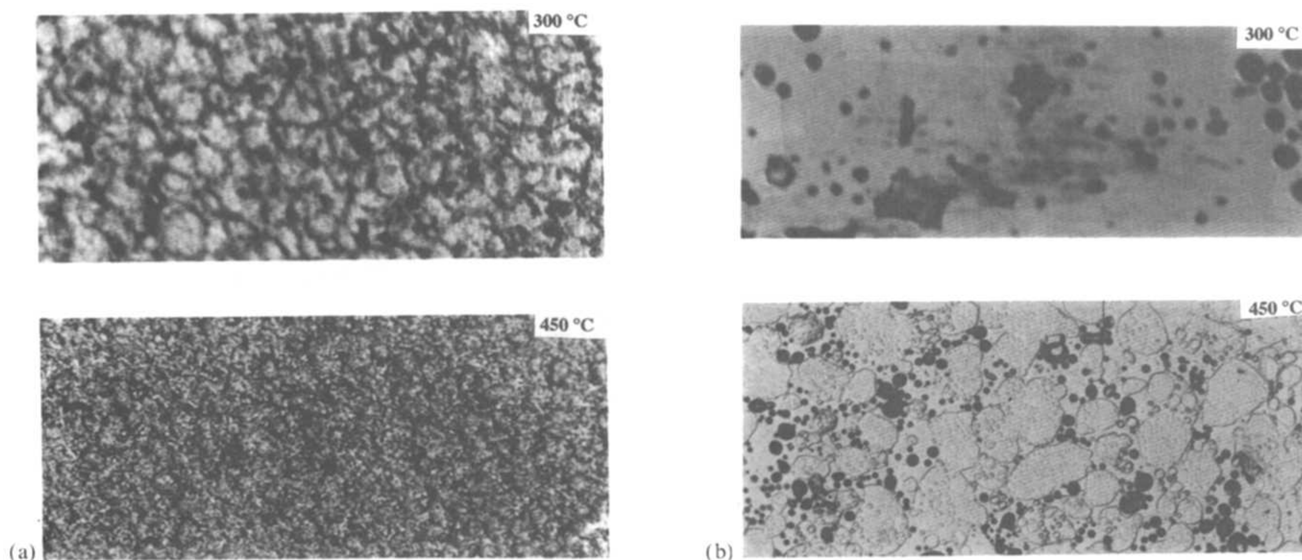

Fig. 2. Optical micrographs of (a) Au/(Ti–W)/diamond samples annealed at 300 and 450 °C and (b) Au/(Ti–W)/silicon samples annealed at 300 and 450 °C.

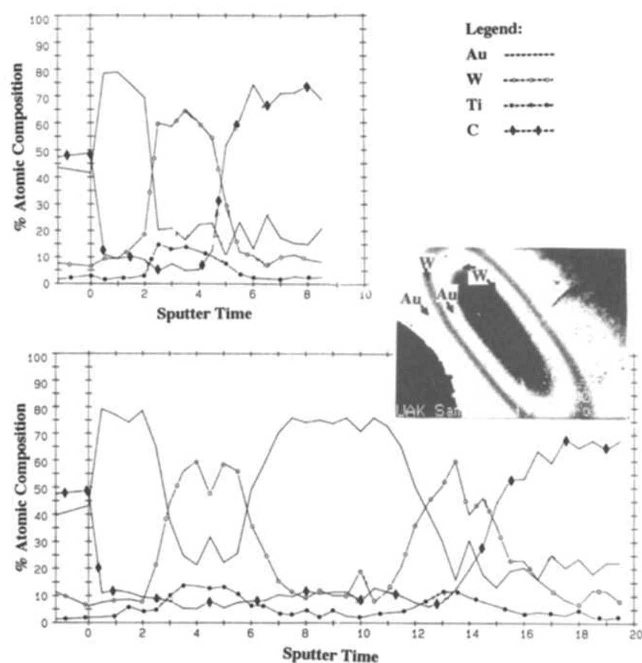

Fig. 3. Compositional Auger depth profiles of Au/(Ti–W)/diamond samples annealed at 150, 300 and 450 °C.

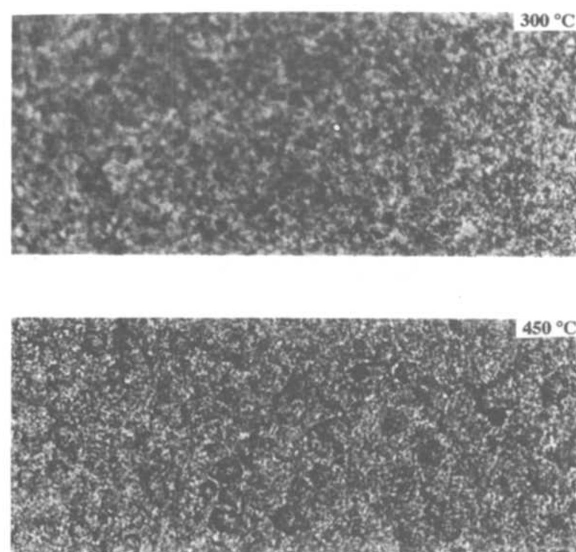

Fig. 4. Optical micrographs of sputtered Au/Cr/diamond samples annealed at 300 and 450 °C.

cause the diamond substrates were breaking beyond this value. Annealing studies on these samples showed some change in the surface of the gold at 450 °C when observed under the optical microscope. The films deposited on silicon also exhibited a change in the color of the surface of the gold layer following annealing at this temperature (Fig. 4). The energy-dispersive spectra showed only the Au Mα characteristic peak and no Cr peak for all the samples. Therefore, although there is some interdiffusion between Cr and Au at 450 °C, it is not extensive enough when compared with the Au/(Ti–W)/diamond samples.

The compositional Auger depth profiles of the samples annealed at 300 and 450 °C are shown in Fig. 5. It can be seen that the Au concentration remains at 85 at.% for both the samples, but the Cr concentration in the Cr region decreased from 65 at.% in the 300 °C sample to 45 at.% in the 450 °C sample. Also, the Au concentration increased from 23 at.% in the 300 °C sample to 45 at.% in the 450 °C sample. Therefore Au has diffused into the Cr layer. The Cr concentration in the surface increased from 5 at.% in the 300 °C sample

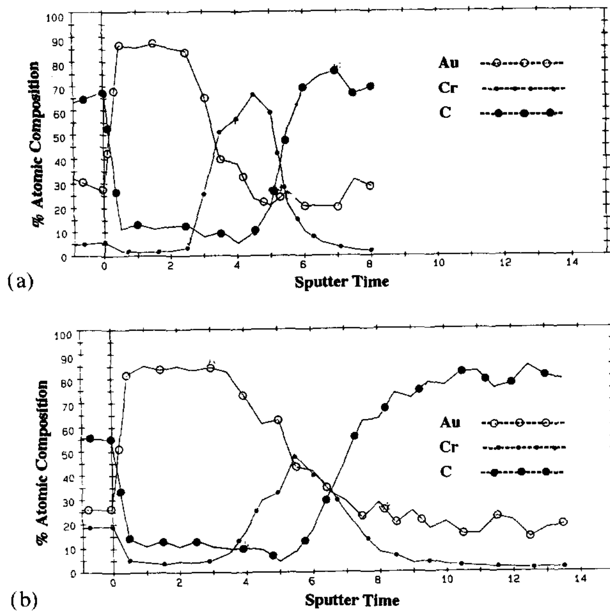

Fig. 5. Compositional Auger depth profiles of sputtered Au/Cr/diamond samples annealed at (a) 300 °C and (b) 450 °C.

to 19 at.% in the 450 °C sample. The Cr concentration in the Au layer also increased from 2 at.% in the 300 °C to 5 at.% in the 450 °C sample. This may be due to the increased amount of Cr in the Au grain boundaries or higher solubility in the bulk Au at higher temperatures. Also, the slope of the C profile decreased considerably in the 450 °C sample when compared with the 300 °C sample. This means that C and Cr interdiffuse at this temperature, possibly forming CrC.

3.3. *Evaporated Au/Cr metallization system*

Adhesion values obtained for the eight experiments as suggested by EChip are shown in Table 2. The deposition rate and total film thickness were varied. Adhesion values up to 11.8 klbf in^{-2} were obtained. The response surface obtained by plotting this data is

Table 2
Adhesion values of evaporated Au/Cr/diamond samples

Deposition rate (Å s^{-1})	Thickness (Å)	Adhesion (klbf in^{-2})
5	5000	4.96
5	3000	11.82
10	5000	9.45
15	5000	9.09
15	1000	10.28
5	1000	9.85
5	5000	5.85
5	3000	11.17

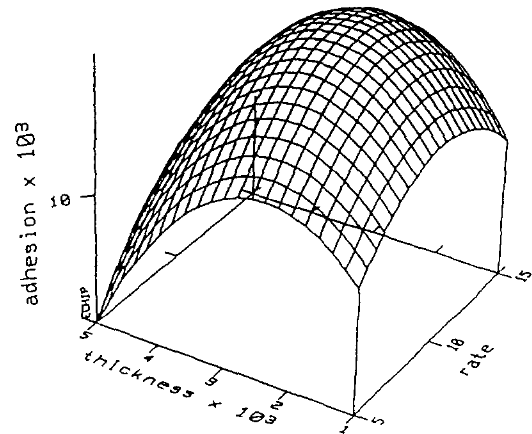

Fig. 6. Response surface of evaporated Au/Cr/diamond samples.

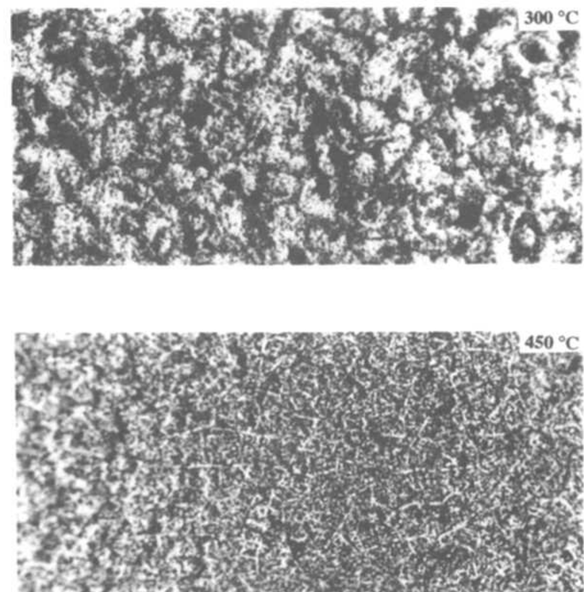

Fig. 7. Optical micrographs of evaportaed Au/Cr/diamond samples annealed at 300 and 450 °C.

shown in Fig. 6. As can be seen from the figure, maximum adhesion is obtained for a film thickness around 3000 Å deposited at a rate of 10 Å s. This corresponds to 2000 Å of Au and 1000 Å of Cr.

Annealing studies did not reveal any change in the surface of the Au layer even for the sample annealed at 450 °C. Similar studies on silicon also did not indicate any change in the surface morphology of the Au layer at this temperature (Fig. 7). This was surprising since sputtered Cr had shown some degradation at 450 °C on diamond as well as Si substrates. This could be due to partial oxidation of evaporated Cr which was deposited at rates of about 10 Å s^{-1} in a vacuum of 1 μTorr (base pressure). As in the case of the sputtered Au/Cr system, energy-dispersive spectra did not reveal any Cr peak even for the 450 °C annealed sample.

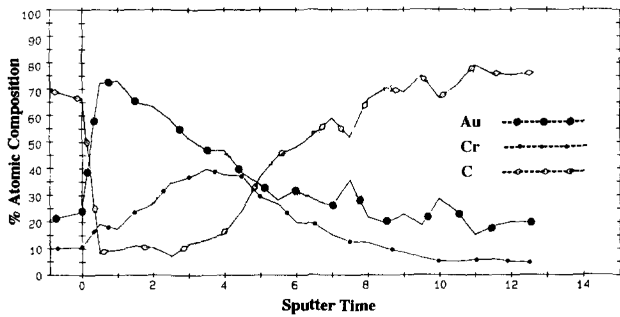

Fig. 8. Compositional Auger depth profile of evaporated Au/Cr/diamond sample annealed at 450 °C.

The compositional Auger depth profile of 450 °C annealed sample is shown in Fig. 8. There was no detectable interdiffusion between Au and Cr at 300 °C. As observed for the sputtered sample, the slope of the C profile at 450 °C indicates dislodging of C atoms into the Cr region. There is only about 10 at.% Cr on the surface of the sample, which explains why both optical microscopy and EDS techniques did not reveal outdiffusion of Cr to the surface. Since the concentrations of Cr and Au are about the same in the Cr region, Cr could be dissolving into the Au and, as a result, very little Cr outdiffuses to the surface. It was observed that below 400 °C there is minimal interdiffusion between Au and Cr whereas, at 450 °C, the interdiffusion occurs but is much less than that observed for either sputtered Au/Cr or Au/(Ti–W) metallization schemes.

4. Conclusions

Adhesion of sputtered Au/(Ti–W) to diamond was found to improve dramatically when the surface was activated by the sputter etch technique. Extensive interdiffusion between Au and Ti–W was found to occur at 450 °C as revealed by optical microscopy, EDS and AES studies. Interdiffusion between Cr and Au, although it occurs at these temperatures, was found to be more subdued compared with Au/(Ti–W). Thus Cr offers better adhesion-promoting and diffusion barrier properties (when compared with Ti–W) for Au-based conductor metallizations on diamond substrates in applications such as MCMs where processing temperatures are limited to 350 °C.

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