ELSEVIER

Thin Solid Films 286 (1996) 264-269

thin solid films

Thermal stability of metallized CVD diamond

C.D. Iacovangelo

Chemical Process Technology Laboratory, GE Corporate Research and Development Center, Schenectady, NY 12301, USA

Received 10 July 1995; accepted 8 November 1995

Abstract

Four metallization systems, WTi/Au, Ti/Pt/Au, Mo/Au and Nb/Au, have been examined for thermal reliability, solderability, wire bonding and adhesion on chemically vapor deposited diamond (CVDD). Thermal stability up to 600 °C was determined by conductivity measurements and X-ray photoelectron spectroscopy depth profiles. WTi/Au was found to be the most thermally stable, exhibiting constant resistivity and little interdiffusion after 4 h at 500 °C. Nb/Au was stable to approximately 450 °C, where marked diffusion of Nb into the gold caused a rapid rise in resistivity and loss of adhesion. Ti/Pt/Au exhibited slow diffusion of Pt into the Au and a modest rise in resistivity as low as 350 °C. Only Mo/Au showed significant interdiffusion between the Mo bond coat and CVDD at such low temperatures. This interdiffusion was markedly enhanced by the presence of oxygen. Each of the four metallization systems initially demonstrated excellent adhesion to CVDD, although all eventually lost adhesion due to conversion of the transition metal carbide bond layer to an oxide.

Keywords: Adhesion; Coatings; Diamond; Diffusion

1. Introduction

Diamond, being the hardest material, has long enjoyed the position of the ultimate material for most cutting and grinding applications. Diamond, however, has several properties which make it an ideal material for electronic applications, the most salient being thermal conductivity (12–18 W cm^{-1} K^{-1}), and dielectric constant (5.7). Currently, chemically vapor deposited diamond (CVDD) has experienced limited market entry primarily as heat sinks for laser diodes [1]. Several investigators are exploring large-area (10 cm × 10 cm) multi-chip modules using CVDD substrates (DSMCMs) to remove the excessive heat that is generated in high-density MCMs [2,3]. In this application, the low dielectric constant, which allows close packing of traces and high speed, is an advantage over AlN or BeO. Transparent CVDD films can make ideal windows for a host of applications ranging from X-rays to microwaves. Diamond can even be doped to provide potential semiconductor properties for passive and active electronic devices that could operate at elevated temperatures. Improvements in process reproducibility and deposition rates over large areas, have brought the cost of CVDD in reach of electronic applications. Each of these applications requires cost effective, reliable methods for metallizing diamond with minimal degradation of thermal and electrical performance.

It has been shown that transition metals can be used as bond layers on CVDD with gold as a top coat for wire bonding and contacts [4,5]. While several authors have recommended these metallizations as ohmic contacts for elevated temperature diamond electronics [6,7], little data exists in the literature on the thermal stability of these metallization systems on CVDD, or their reliability for wire bonding and solder die attach. Katz et al. have shown that the state of the art Ti/Pt/Au metallization system can be used to die attach InP chips to CVDD with thin film solder as deposited but no information was given as to thermal reliability [8]. Katz et al. have also shown that Ti/Ni/Au can overcome the problem of Pt reaction with the Sn in AuSn solders but again no information was given as to thermal stability of these systems. In many applications such as MCMs, the diamond substrate must go through several thermal cycles often up to an hour at 350 °C, with repeated exposure when repairs are needed. This puts a significant thermal stability requirement on the metallization system of choice and can dramatically limit the application for many of the standard metallization systems such as Ni/Au [9]. It is critical, therefore, that metallization systems on CVDD be developed that can withstand long durations in air at elevated temperatures and remain solderable, well adherent, and wire bondable. We will show data for three metallization systems that demonstrate this reliability.

0040-6090/96/$15.00 © 1996 Elsevier Science S.A. All rights reserved
SSDI 0040-6090(95)08236-0

2. Experimental

All experiments were conducted on square CVDD plates approximately 2.54 cm on a side and approximately 0.025 cm thick. The CVDD was mechanically polished with diamond grit to approximately 300 Å R_a. The diamond was cleaned in boiling acids, rinsed in deionized water, and dried in methanol and propanol prior to deposition. The CVDD was sputter etched for 6 min at 100 W prior to deposition. All metals were d.c. magnetron sputtered in a Plasma Science ARC unit at 0.5–2.2 Pa argon. The background pressure was typically 2×10^{-7} Pa prior to sputtering. The four transition metal bond coats Ti, WTi, Mo, and Nb were deposited at 5 W cm^{-2}. Platinum and gold were deposited at 2.5 W cm^2. The target to substrate distance was approximately 7.5 cm which resulted in deposition rates of 45, 65, 48, 60, 75 and 90 nm min^{-1} for Ti, WTi, Mo, Nb, Pt and Au respectively. The WTi was sputtered from a 90:10 alloy target and the composition of the deposit was analyzed with AA and ICP. As shown in Fig. 1, the deposits were 8% Ti and independent of sputtering power or pressure. The stress of the deposit, however, was highly pressure dependent. Fig. 1 shows the intrinsic stress in the deposit as a function of Ar sputtering pressure. The deposits used in these studies were deposited at 1.2 Pa with a slight compressive stress. The conductivity of the bond coats, shown in Fig. 2, was independent of pressure for the WTi coating. The resistivity of Nb and Ti, however, increased with pressure, presumably due to incorporation of gas into the deposit. For this reason, the deposits were sputtered at lower gas pressures. Unless otherwise stated in the text, all heat treatments were carried out in air. Temperatures were controlled to ±2 °C using a Love® controller with a type-K thermocouple. Adhesion was measured with a Sebastian tensile adhesion tester using epoxy coated pull pins with a stress limit of 69 MPa. The metallization was patterned into 0.25 cm wide by 2.54 cm long strips for conductivity measurements. Measurements were made using a Keithley Model 224 current source, Keithley Model 19A multimeter, and a Dumas Model C45 4 point probe. Values given are the average of 3–6 readings for each metallization system. X-ray photoelectron spectroscopy (XPS) surface analysis was obtained using a Physical Electronics Model PHI-45. Depth profiles were obtained by sputter etching at approximately 5 nm min^{-1} using 2.8 kV argon ions. Wire bonding was performed with 3.3×10^{-3} cm gold wire using a K&S model 1926 wire bonding station and a Micro Tester Model BT22 pull tester.

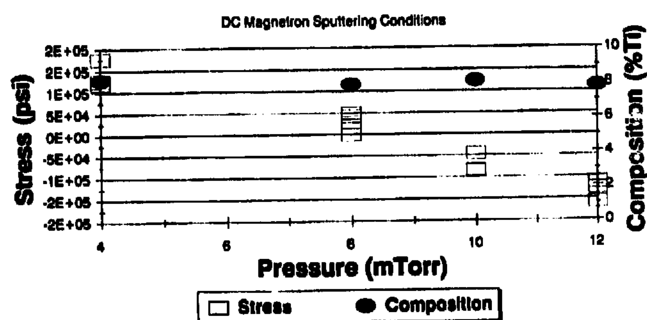

Fig. 1. Composition and stress of WTi deposits on CVDD as a function of argon sputtering pressure.

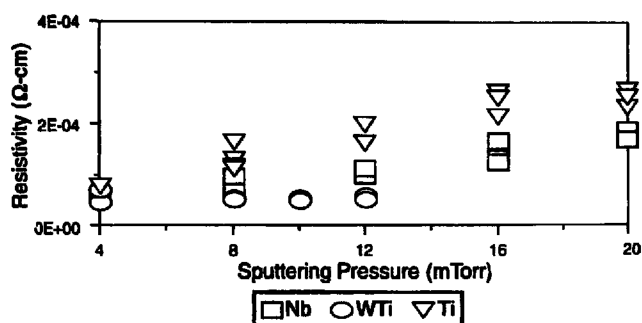

Fig. 2. Resistivity of sputtered bond coats on CVDD as a function of argon sputtering pressure.

3. Results and discussion

Most metallization systems on CVDD depend upon transition metals to bond to diamond through the formation of transition metal carbides at the metal/CVDD interface. Earlier [10], we demonstrated excellent adhesion of Cr, Nb, Ti, W, and WTi as bond coats deposited by a variety of techniques including sputtering, pack CVD [11], low-pressure CVD (LPCVD) [12], and electroless plating. Electronic applications require the metallization to undergo a variety of thermal excursions from a few hundred degrees to as high as 500 °C (e.g. die and seal ring attachment, lid sealing, and lead attach) and remain conductive and oxide free so that reliable soldering and wire bonding can be performed. In this paper we examined the thermal reliability of four metallization systems on CVDD: Ti/Pt/Au 100/200/500 nm, WTi (90/10)/Au 100/500 nm, Mo/Au 100/500 nm, and Nb/Au 100/500 nm. The Ti/Pt/Au was chosen because of its copious use in the CVDD community as an industry standard. This metallization, however, is expensive, difficult to pattern because of the Pt, and interacts with AuSn solder in a detrimental manner [8]. Niobium is unique among the transition metals in that the carbide is readily dissolved in aqueous solutions. Nb/Au was, therefore, selected for the ease of patterning the NbC bond layer by wet etching. Nb has been used in a few applications as a barrier between Au and Al, however, the authors did not show data on the transport of Nb into the gold at these temperatures [13]. Like Nb, WTi has been used extensively as a barrier to Al transport [14] for ceramic packaging. Recently, Naseem et al. [5] showed thermal reliability of WTi/Au on CVDD up to 450 °C. Mo/Au has been used extensively for high-temperature CVDD applications as an active device. Interesting though, most authors do not report any long term stability data even though the intended use is a high temperature application. Rosen et al. [15] have shown that excellent ohmic contacts can be maintained up to 130 h in low P_{O2} argon atmospheres.

The stability of these metallizations to thermal processing was examined by monitoring the conductivity of patterned metal stripes after heat treating for up to 4 h from 300 to 600 °C in air. XPS depth profiles were performed, generally after 4 h at each temperature. Plotted in Fig. 3 is the resistivity of WTi/Au, Ti/Pt/Au and Nb/Au metallizations after heat treating from 300 to 600 °C. As shown, all three metallizations demonstrated good stability to processing at 300 °C for 4 h with no increase in resistivity. XPS depth profiles showed no grain boundary diffusion of the bond coats into the gold and pull tests showed no deterioration in adhesion; all coating exceeded 69 MPa. At 400 °C, the Ti/Pt/Au standard showed a marked rise in resistivity compared with WTi/Au and Nb/Au, which showed no increase in resistivity. In fact, these metallizations demonstrated a slight improvement in conductivity at 400 °C. The XPS depth profiles of Fig. 4 show the rise in resistivity to be due to Pt diffusion into the gold. No Nb diffusion into the gold was apparent after this thermal excursion. Likewise, the WTi sample showed no detectable transport of Ti out of the alloy. There was a slightly higher oxygen content but this was also seen in the as-deposited sample. By comparison, a pure Ti layer would have shown significant diffusion through the gold, resulting in a several hundred angstrom thick titanium oxide coating [16]. Tungsten which is the slower diffusing metal through gold, was not observed.

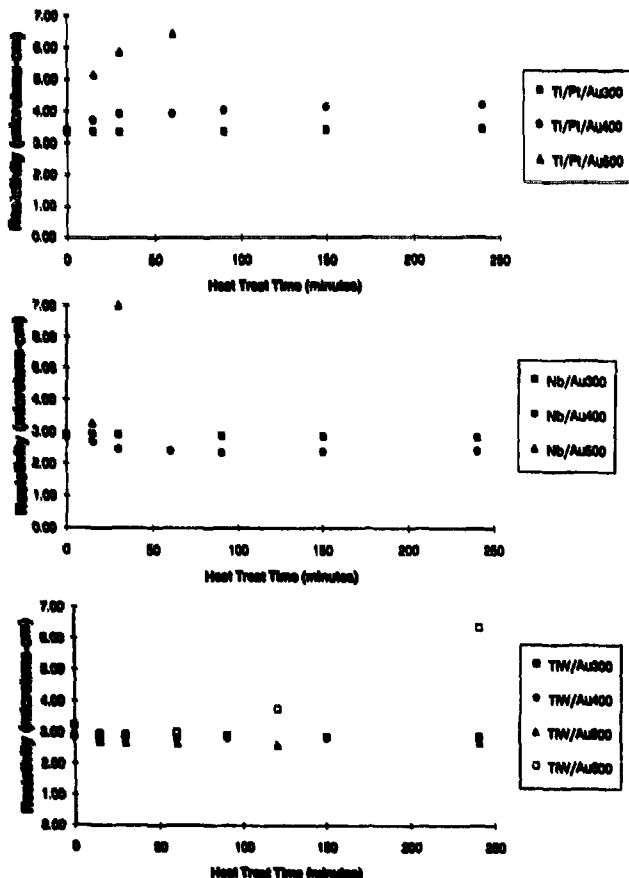

Fig. 3. Electrical resistivity of sputtered coatings on CVDD after heat treating in air from 300 to 600 °C.

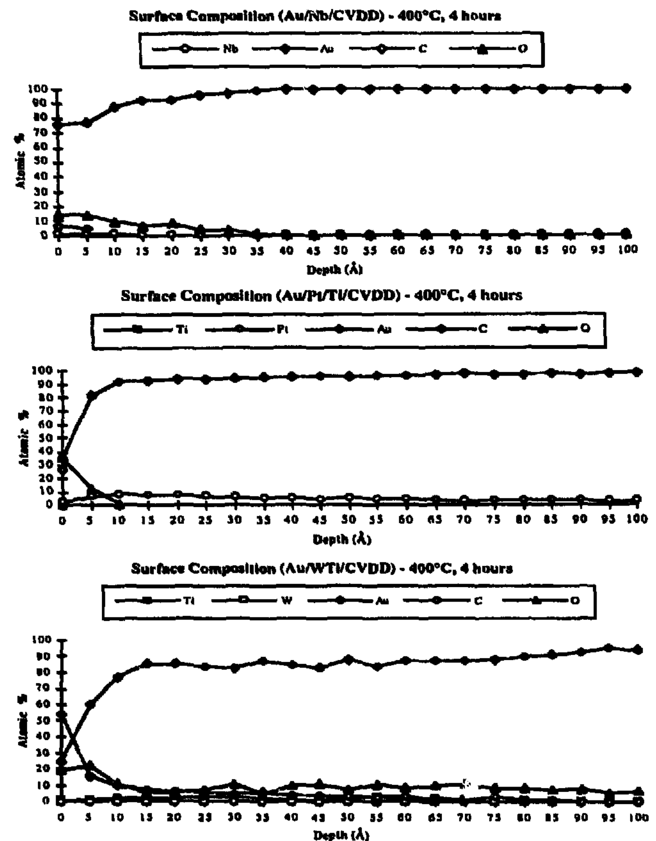

Fig. 4. XPS depth profile of sputtered coatings on CVDD after heat treating in air for 4 h at 400 °C.

At 500 °C, both the Ti/Pt/Au and Nb/Au samples had a catastrophic rise in resistivity due to the transport of Pt and Nb into the gold; as shown in Fig. 5. Both samples also exhibited marked oxidation of the diffused metal. This effect was dramatic for the Nb sample which exhibited oxidation through the entire sample sufficient to decarburize the NbC bond layer and cause delamination of the metallization. As shown, the WTi/Au sample remained stable through 4 h at 500 °C with no interdiffusion or degradation in adhesion.

These results do not agree with those of Naseem et al. [5], who found significantly more interdiffusion of the WTi into the Au at these temperatures. The exact cause of this discrepancy is unknown. One possibility is the activity of Ti in the alloy. The marked increase in stability of the alloy versus a pure Ti layer is due to the decreased activity of Ti in the deposited alloy. It should be noted, however, that the Ti activity in the deposit can be markedly different from the target depending upon the sputtering conditions, distance from the target, and geographical position relative to the center of the target. This is due to the large difference in mass between the W and Ti ions. The samples used in this study were placed directly under the center of a round target with no motion of the substrate so that no significant variation in W:Ti occurred within the 2.5 cm square. Since no data was given for the composition of the deposit in Ref. [5], it is possible that the deposit was richer in Ti, which would

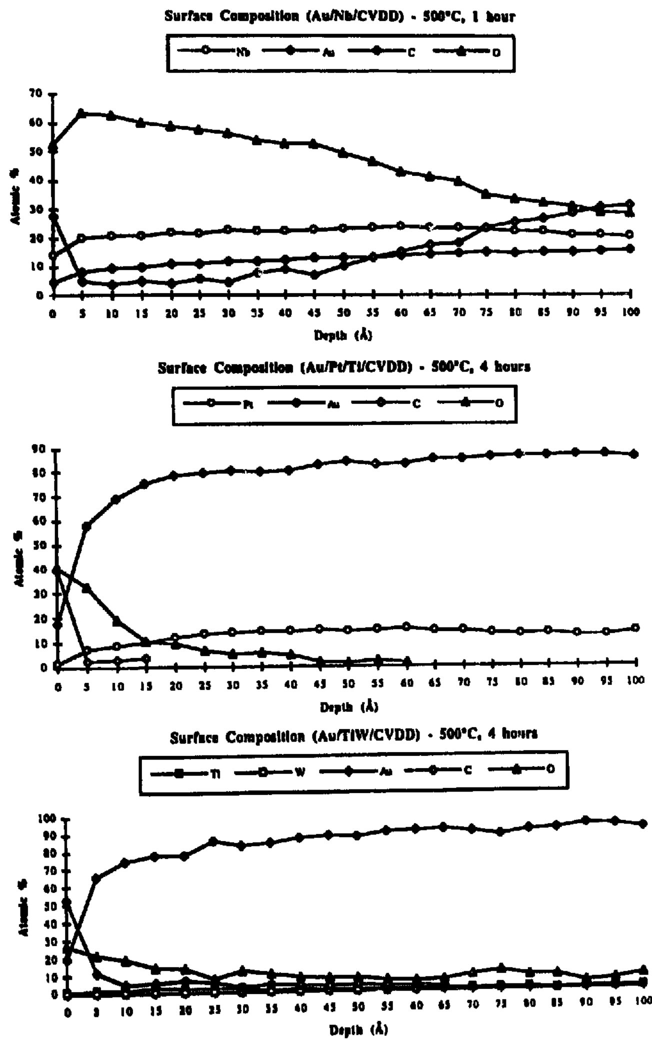

Fig. 5. XPS depth profile of sputtered coatings on CVDD after heat treating in air for 4 h at 500 °C.

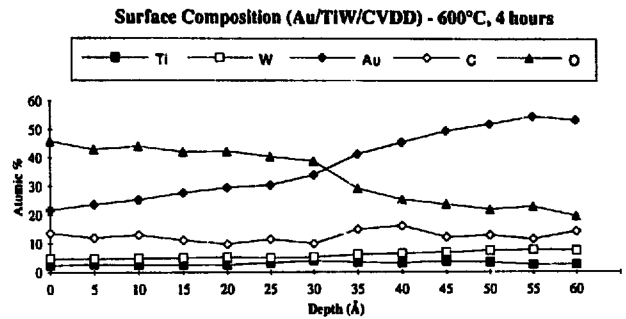

Fig. 6. XPS depth profile of sputtered Au/WTi coatings on CVDD after heat treating in air for 4 h at 600 °C.

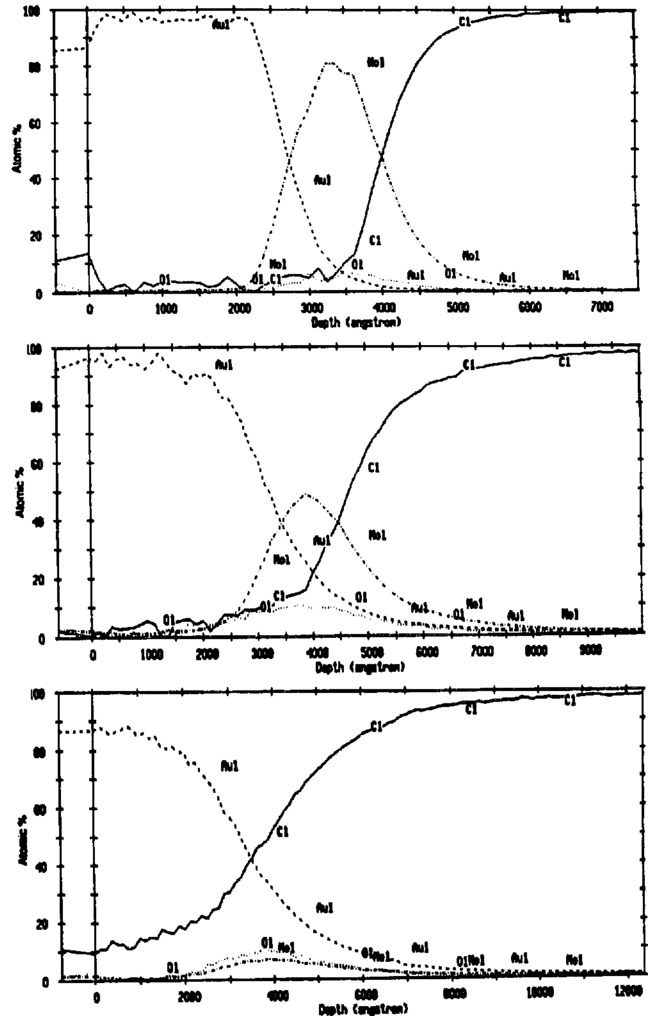

Fig. 7. XPS depth profile of Mo/Au coatings on CVDD: top, as sputtered; middle, after heat treating in air for 4 h at 450 °C; bottom, after heat treating in air for 4 h at 550 °C.

decrease its thermal stability but enhance its adhesion to CVDD.

The WTi/Au sample remained stable through 1 h at 600 °C; as shown in Fig. 6. After 4 h, however, the resistivity doubled because of excessive oxidation. Like the Nb sample, this oxidation penetrated through to the carbide bond layer causing delamination of the metallization.

The results for Mo/Au metallization of CVDD were dramatically different than the other three transition metal bond coats. Shown in Fig. 7 are XPS depth profiles from the Au surface through to the CVDD on as-deposited coatings and after 4 h at 450 and 550°C. The disappearance of the Mo interface is quite striking. XPS analysis also shows a significant increase in oxidation of the Mo with increasing temperature. The previous samples demonstrated classic grain boundary diffusion of the transition metal through the gold with little measurable diffusion into the CVDD. Mo, in contrast, showed massive migration into both the Au and the CVDD. We have not observed this phenomena with any other transition metal.

This test was repeated with a modification that the entire CVDD was coated with Mo and only the Au was patterned for conductivity measurements. This insured that the Mo layer was unperturbed by the Au deposition process. XPS depth profiles of an area where the gold was removed leaving only the Mo showed that the Mo had migrated deep into the CVDD. The test was repeated in a 4% hydrogen/argon environment to examine the effect of oxygen on molybdenum oxidation and interdiffusion. Fig. 8 shows that very little Mo diffusion into either the gold or CVDD occurred without the presence of oxygen.

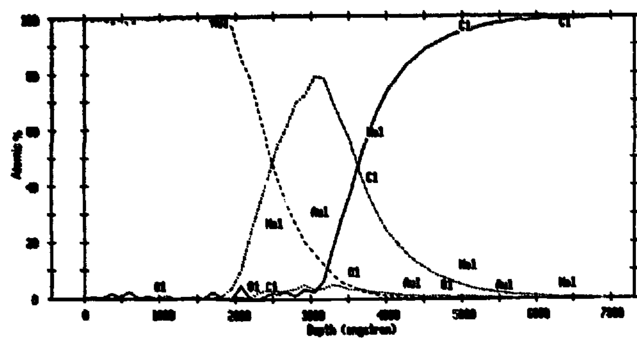

Fig. 8. XPS depth profile of Mo/Au coatings on CVDD after heat treating in 5%H_2/Ar for 4 h at 550 °C.

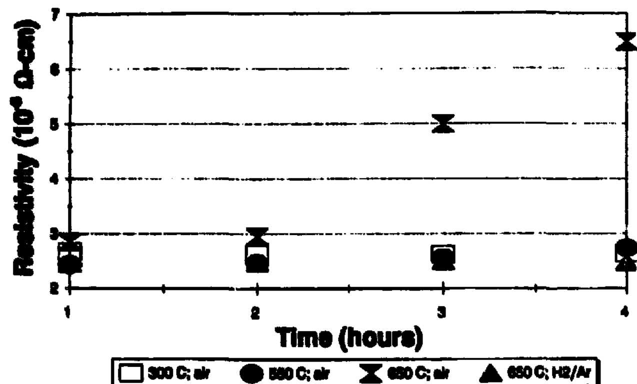

Fig. 9. Electrical resistivity of Au/Mo/CVDD metallization after heat treating in air and 4% H_2/Ar.

The resistivity change with time at temperature for samples treated in air and hydrogen/argon are shown in Fig. 9. In the reducing environment the resistivity was unchanged through 4 h at 550 °C, as observed by Rosen et al. In air, however, the resistivity rose dramatically at temperatures as low as 350 °C, corresponding to the interdiffusion shown in Figs. 7 and 8. These results demonstrate the critically of any processing of the diamond in air prior to hermetic sealing and the need for extremely low P_{O2} hermetic seals when this metallization is used.

Wire bond tests after 4 h of heat treating on WTi/Au and Ti/Pt/Au samples using 3.3×10^{-3} cm Au wire are shown in Fig. 10. The WTi/Au samples had a mean of 12.9 and 13.3 g at 400 °C and 500 °C respectively, with a standard deviation of 0.6 g. Most of the pulls resulted in wire failure rather than separation from the substrate. The Ti/Pt/Au sample showed a decrease in mean pull strength from 14.2 to 12.6 g, and a slight increase in standard deviation to 1.5 g from 400 °C to 500 °C. Several of the breaks occurred at the wire/metallization interface. Tensile pull tests showed no decrease in adhesion of either metallization to the CVDD after 4 h at 500 °C. No observable increase in carbide formation was observed for any of the four metallizations.

4. Conclusions

Three of the four sputtered coating systems examined provided thermally reliable thin film metallization on CVDD:

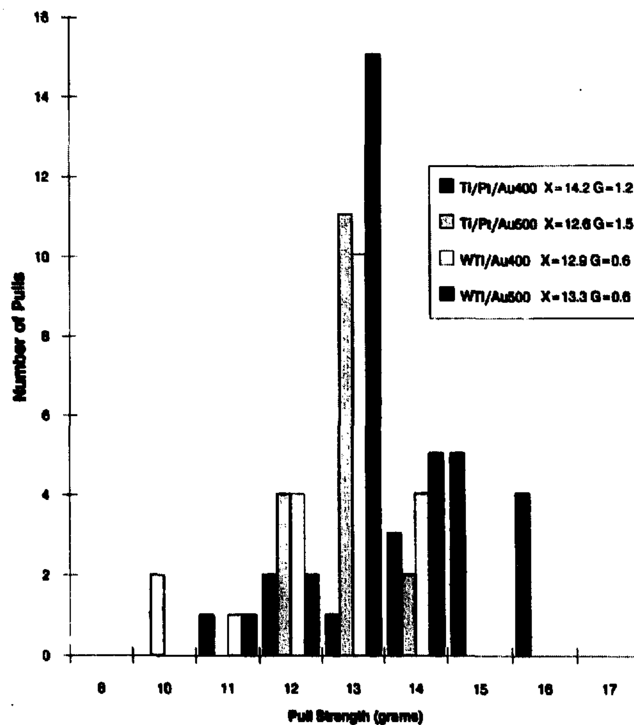

Fig. 10. Pull strength of 3.3×10^{-3} cm gold wires after heat treating for 4 h at 400 and 500 °C.

Ti/Pt/Au, WTi(90/10)/Au, and Nb/Au. All three demonstrated excellent adhesion to CVDD and stability to elevated temperature processing in air up to 300 °C for 4 h. The Nb/Au metallization was more stable than the Ti/Pt/Au industry standard at 400 °C but degraded rapidly at 500 °C due to interdiffusion and oxidation of the Nb. The WTi/Au metallization had the best performance, remaining stable at 550 °C for up to 4 h. After 1 h at 600 °C, this metallization also failed because of Ti transport out of the WTi. Both the Ti in the gold and the TiC bonding the metallization to the CVDD oxidized, causing poor performance and delamination from the CVDD. All three metallizations provided adequate thermal stability for most electronic applications. The optimum metallization will depend on other factors such as solder compatibility, cost, ease of patterning, oxidation resistance, etc.

The Mo/Au metallization system behavior in air was unique among the systems studied. While the performance in reducing environments was extremely stable up to 600 °C, the performance degrade rapidly in air at temperatures as low as 350 °C. Oxidation of the Mo resulted in an excessive rise in resistivity and massive diffusion of the Mo into both the Au and CVDD layers.

Acknowledgements

The author wishes to acknowledge the assistance of J. Chera for XPS analysis, K. Borst, L. Gruenke, and D. Skelly for sputtering, and E. Jerabek and P. DiConza for their constant help and fruitful discussions. The author also wishes to

acknowledge J. Pagois for manuscript preparation, and GE Superabrasives for supplying CVDD test samples. The author gratefully acknowledges NRL for administering and ARPA for the financial support of this work under contract #N00014-91-C-2167.

References

[1] AT&T, The world's first commercial application of a novel synthetic diamond material combined with an advanced metallization bonding technique, *Wall Street J., B9* (1992).

[2] General Electric, Development of free standing diamond manufacturing technology for thermal management substrates, *ARPA #N00014-91-C-2167.*

[3] R.C. Eden, Applicability of diamond substrates to multi-chip modules, *Int. Soc. Microelectronics Proc. 1*, INSIM, Reston, VA, 1991, pp. 363–367.

[4] Jiang Xiang-Liu et al., Diamond Optics V, *SPIE, 1759* (1992) 145–153.

[5] N.A. Naseem et al., *Int. J. Microcircuits Electron. Packaging, 16*(4) (1993) 257–268.

[6] J. Nakanishi et al., *J. Appl. Phys., 76*(4) (1994) 2293–2298.

[7] K.L. Moazed, J.R. Zeilder and M.J. Taylor, *Mater. Res. Soc. Symp. Proc., 162* (1990) 347–352.

[8] A. Katz, C.H. Lee and K.L. Tai, *Mater. Chem. Phys., 37* (1994) 303–328.

[9] C.D. Iacovangelo, New autocatalytic gold bath and diffusion barrier coatings, *AESF SUR/FIN'92, Inter. Tech. Conf. Proc., Atlanta, GA, June 22–25*, AESF, Orlando, FL, Vol. 1, 1992, p. 51.

[10] C.D. Iacovangelo and E.C. Jerabek, Metallizing CVD diamond for electronic substrates, *Int. Soc. Microelectronics Proc., Dallas, TX*, ISNIM, Reston, VA, 1993, pp. 132–137.

[11] D.S. Park, *US Patent No. 4 664 991*, June 15, 1967.

[12] C.D. Iacovangeo, E.C. Jerabek and R.H. Wilson, *US Patent No. 5 328 715*, June 12, 1994.

[13] B.L. Doyle et al., *J. Appl. Phys., 53*(9) (1982) 6186–6190.

[14] J.M. Oparowski, R.D. Sisson and R.R. Biederman, *Thin Solid Films, 153* (1987) 313–328.

[15] M. Rosen, C.A. Hewett, K.L. Moazed and J.R. Zeidler, *J. Electrochem. Soc., 139*(7) (1992) 2001–2004.

[16] R.S. Nowicki et al., *Thin Solid Films, 53* (1978) 195–205.