Diamond & Related Materials 39 (2013) 65–72

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Diamond CVD film formation onto WC–Co substrates using a thermally nitrided Cr diffusion-barrier

E. Hojman [a],*, R. Akhvlediani [b], A. Layyous [c], A. Hoffman [a,b],**

[a] Russell Berrie Nanotechnology Institute, Technion, Haifa 32000, Israel
[b] Schulich Faculty of Chemistry, Technion, Haifa 32000, Israel
[c] Iscar Ltd., P.O. Box 11, Tefen 24959, Israel

ARTICLE INFO

Article history:
Received 10 June 2013
Received in revised form 25 July 2013
Accepted 14 August 2013
Available online 22 August 2013

Keywords:
Diamond film
Hot filament CVD
Chromium nitride
Diffusion barrier

ABSTRACT

Diamond film deposition onto WC-Co substrates exhibits several limitations regarding the final diamond quality in the film and its adhesion due to the chemical interaction between the Co in the substrate and the diamond CVD environment. In the present study, the use of a ~1.5 μm thermally nitrided Cr interlayer was examined as an effective diffusion barrier throughout the CVD process. Nitridation of the Cr PVD layer in NH_3 environment resulted in the formation of a graded CrN/Cr_2N layer comprised mainly of the CrN phase, accompanied with the formation of a porous 'net-like' microstructure at the surface. During both thermal nitridation and exposure to the CVD environment up to 360 min, the diffusion of C and Co from the substrate into the interlayer was limited to the region adjacent to the Cr–N interlayer/WC–Co substrate interface, which contained the Cr_2N phase. In this region, the Co interacted with the Cr lattice to form a CoCr phase, which was suggested to enhance the chemical binding between the interlayer and the substrate. The region containing the CrN phase was suggested to act as an effective diffusion barrier due to its fully occupied interstitial sites and relatively high crystalline density compared to the underlying Cr_2N phase. It was evident that the deleterious effects of Co during the CVD process were successfully suppressed using the Cr–N interlayer and the deposited diamond film exhibited improved adhesion and higher diamond quality.

The formation of phases within the interlayer during nitridation and the diamond CVD process, and diamond quality evaluation in the deposited films were investigated by complementary techniques: SEM, XRD, XPS, SIMS and Raman spectroscopy.

1. Introduction

Diamond films grown by chemical vapor deposition (CVD) methods onto cemented WC–Co are a most promising candidate for machining application due to their extreme hardness, and chemical and wear resistance [1]. 5–12 wt.% of Co serves as a binder phase in the fabrication process of the cemented WC substrate and provides additional toughness to the cemented composite [2]. The performance of diamond film-coated WC–Co as machining tools, however, is limited by the coating–substrate adhesion. From this point of view, the main parameters that hinder the adhesion of such a coated system are: (1) the thermal stresses that build-up during temperature changes due to the mismatch in thermal expansion coefficients (CTEs) of diamond and WC–Co; and (2) the formation of non-diamond sp^2-bonded carbon structures within the diamond film and at the interface associated with the catalytic interaction of Co with the active carbon species involved in the diamond CVD environment [3–7]. The general methodology for adhesion enhancement relates to modification of the substrate's morphological and chemical properties at its surface region prior to deposition of the diamond film. The two most discussed approaches in the literature are related to either cobalt removal from the topmost 3–10 μm of the substrate by chemical etching methods [8–11] or by using an appropriate interlayer to suppress the interaction between Co and the diamond CVD environment [12–15].

Although the approach of cobalt removal partially avoids its deleterious influence during the CVD process, it results in a decrease of the toughness and embrittlement of the underlying WC–Co substrate [16]. Alternatively, if appropriately selected, the interlayer is expected to act as a diffusion barrier for Co, to reduce the CTE mismatch by having an intermediate thermal expansion property, and to enhance the adhesion to both the diamond film and the WC–Co substrate.

The approach of interlayer deposition required the study of different materials, such as amorphous carbon [17,18], metallic materials (e.g. W, Ag, Ti, Cr) [19–21] and ceramics (e.g. SiC, TiC, WC, Si_3N_4, TiN) [22–24]. Among these interlayer materials, the study of nitrides in general and

---

* Corresponding author. Tel.: +972 4 8293754, +972 4 8293747; fax: +972 4 8295703.
** Correspondence to: A. Hoffman, Russell Berrie Nanotechnology Institute, Technion, Haifa, 32000, Israel.
E-mail addresses: eladhoj@tx.technion.ac.il (E. Hojman), choffman@tx.technion.ac.il (A. Hoffman).

0925-9635/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.diamond.2013.08.002

of Cr–N in particular as diffusion barriers for Co were recently reported. Petrikowski et al. [25] showed that under a 60 h heat treatment in a H_2 atmosphere and temperature of 765 °C (in a HFCVD reactor), a high amount of Co diffusion was allowed through the Cr–N interlayer (1 μm thick). Similarly, in another study by Manaud et al. [26], Cr–N interlayers of 1–2 μm were found to allow complete diffusion of Co after 5 h of diamond deposition at a temperature of 880 °C (in a microwave CVD reactor). In these studies, as well as in other reports [14,15] the Cr–N interlayer was deposited using PVD methods, such as DC magnetron sputtering and cathodic-arc ion plating, which involve sputtering of a pure Cr target in an Ar–N_2 gas mixture atmosphere. However, as reported by Shen et al. [27], in a similar case of deposition of W–N films, the N_2 molecules involved in the PVD process induced a suppressing effect on the formation of a crystalline structure. This was proposed to occur due to the trapping and roadblocking effects of the N_2 molecules on the mobility of the metal particles, thus hindering their migration into preferred sites for crystallization growth.

From this point of view, the deposition of the Cr–N interlayer through an equilibrium process, which involves diffusion of N atoms into a crystalline Cr layer at elevated temperatures, may contribute to the crystalline structure of the layer and thereby to its properties as a diffusion barrier for Co. Thermal nitridation of Cr carried out by exposure to a NH_3 (or N_2) atmosphere at temperatures of above 600 °C is known to allow the formation of Cr–N phases through an equilibrium process. This method was formerly used to increase the surface hardness of Cr containing steel alloys [28–30] and more recent reports deal with its use on Cr coatings for tribological property enhancement [31–35]. Previous studies initially reported by Glozman et al. [36–39] found that such a Cr–N interlayer performed as an effective diffusion barrier for C and Fe during diamond film deposition onto steel substrates.

In the present work, we examine the effectiveness of a Cr–N layer, produced using thermal nitridation of a PVD ~1.5 μm Cr layer, as a diffusion barrier between WC–10%Co substrates and diamond CVD films. The diamond CVD was carried out using the hot-filament method. We focus on the morphological and chemical properties of the layer, obtained following thermal nitridation in a NH_3 environment; on the chemical influence of the CVD environment on the Cr–N layer; and on the quality of the deposited diamond film compared to direct deposition onto WC–10%Co substrates. Phase formation in the interlayer during nitridation and the diamond CVD process and diamond quality evaluation in the deposited films were investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS) and Raman spectroscopy.

2. Experimental

2.1. Sample preparation

Commercial WC–Co inserts with a nominal Co bulk content of 10 wt.% and a grain size of 1 μm were used as substrates (produced by Iscar Ltd., Israel). Following a surface cleaning process by sand-blast polish (with Al_2O_3 powder) and acetone cleaning in an ultrasonic bath, the substrates were coated with a Cr layer of about 1.5 μm thick, by a magnetron sputtering PVD method. The PVD was performed in an industrial reactor (Von Ardenne-LS 320 S) at a deposition temperature of 150 °C for 60 min, under a working pressure of 9×10^{-3} Torr, a DC power of 200 W and an Ar^+ ion flow rate of 20 sccm. Nitridation of the Cr layer was then carried out in a 100 sccm NH_3 flow at a system temperature of 800 °C and pressure of 200 Torr for 60 min. Following nitridation, the samples were ultrasonically abraded for 40 min in a 10 ml acetone suspension containing a mixed powder slurry of 0.2 g diamond (<0.25 μm) and 0.2 g titanium (44–100 μm) particles. This step is aimed to enhance diamond nucleation density by introducing precursor diamond nucleation sites and it is commonly referred as 'seeding' [40–42]. Diamond deposition was performed using a hot-filament CVD (HF-CVD) reactor with a CH_4 to H_2 gas mixture of 1:99 vol.%, total gas flow rate of 100 sccm and working pressure of 50 Torr. In the reactor, the samples were placed on a molybdenum holder that was heated to 650 °C and placed 8 mm below a rhenium filament heated to 2000 °C that was used for gas activation. The temperatures of the heated sample holder and filament were monitored by a chromel–alumel thermocouple placed below the holder and an optical pyrometer, respectively. In several cases, the samples were subjected to the CVD process (with same parameters as described above) for 30 min, without prior seeding. This type of treatment is referred in this work as 'carburization'.

2.2. Characterization methods

The surface morphology of the Cr layer and nitrided Cr layer was examined by Scanning Electron Microscopy (SEM) using a FEI E-SEM Quanta 200 type microscope. X-ray Diffraction (XRD) was used for the characterization of crystalline phases within the coated system, which may have formed upon nitridation and diamond CVD processes. The XRD spectra were recorded in a 2θ range of 30–70° with a Rigaku MiniFlex X-ray diffractometer using a Cu X-ray tube (Cu-Kα radiation with $\lambda = 1.54$ Å) operated at 30 kV and 15 mA. Determination of the crystalline phases in the samples was done by 'MATCH' software (Crystal Impact, Germany). Composition and chemical bond-configuration at the near-surface region was investigated by X-ray photoelectron spectroscopy (XPS) using a SPECS phoibos 150-MCD spectrometer equipped with a hemispherical electron analyzer (operated at pass energy of 32 eV) with unmonochromatized Al Kα radiation as the excitation source (1486.6 eV, 10 mA, 10 kV). The work function was calibrated to give a binding energy of 83.96 eV for the Au ($4f_{7/2}$) XP peak for a metallic gold sample. The base pressure in the analysis chamber was approximately 10^{-9} Torr. Surface cleaning was conducted by Ar^+ sputtering for 30 min (2 kV). Quantitative analysis of the XP spectra was done using the CasaXPS software [43] considering the provided sensitivity factors and background subtraction according to the Shirley method. Depth profiling by secondary ion mass spectrometry (SIMS) was performed in dual-beam mode using an IonTOF-5 apparatus at a basic chamber pressure of 10^{-10} Torr. A 2 keV Cs^+ sputter beam was rastered over a sampling area of 75 × 75 μm. A 25 keV Bi^+ analysis beam was used for collection of secondary M^- ions. A 20 eV electron beam was switched on during the sputtering for charge compensation. The estimated depth scale was calculated according to the sputtering rates obtained in the diamond film and interlayer, which resulted in 0.358 and 0.317 nm/s, respectively. Note that although the depth resolution deteriorated mainly due to the initial sample roughness, the SIMS results could be compared on a relative scale because the measurement parameters were kept constant. The presence of diamond and other carbon solid phases was determined by Raman spectroscopy using a micro-Raman DILOR XY system configured with a focused Ar laser beam ($\lambda = 514.5$ nm) with an output power of 3 mW and a diameter of approximately 2 μm. The Raman spectra were collected in the 1000–1800 cm^{-1} range. Raman spectroscopy was also employed for determination of residual stresses in the deposited diamond films.

3. Results

3.1. Characterization of the thermally nitrided Cr PVD layer

The Cr PVD layer deposited onto the WC–10%Co substrate was about 1.5 μm thick and following the nitridation process in NH_3 environment a change in both microstructure and chemical properties was observed. Fig. 1 displays the plain view SEM images (BSE mode) of the Cr layer surface, as deposited and after nitridation for 60 min at 800 °C. The rough surface morphology of the deposited Cr layer (prior nitridation) shown in Fig. 1a, consists of a well-defined faceted polycrystalline microstructure. Throughout the nitridation, the surface morphology changed into a porous 'net-like' microstructure with no defined