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Diamond and Related Materials 8 (1999) 155–159

DIAMOND AND RELATED MATERIALS

Early stages of carbon film growth: carbide interface formation on molybdenum

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Received 27 July 1998; accepted 12 November 1998

Abstract

In this study we present an investigation of the carbide formation and early stages of carbon film growth using a low energy carbon beam to supply the growth species. Carbon is supplied through electron beam evaporation of graphite and between 0.1 and 40 ML are deposited on a molybdenum substrate (substrate temperature 400 °C). Photoelectron spectroscopy in the ultraviolet and X-ray regime was employed to characterize the surface and observe the carbide and carbon film formation. Two regimes, with respect to the surface composition, can be identified: firstly, the carbide formation, and, secondly the growth of a pure carbon overlayer. A carbide interface with Mo_2C stoichiometry is created, and the formation of a pure amorphous carbon layer is observed for carbon coverages exceeding about 3.4 ML. But even after the onset of carbon film growth, the carbide interface growth is not terminated, and the extension of the carbide region into the bulk continues to increase. Diffusion through the carbide interface is still present and a dynamic rather than static interfacial layer exists. The diffusion of carbon through the metal carbide dominates the interface formation, which is also evidenced by a delayed onset of carbon film formation at 600 °C. Apart from the observation of interface formation, this experiment also enabled us to observe the valence band spectrum of molybdenum carbide (Mo_2C) for the first time. The sequential deposition of carbon was shown to be a suitable method to produce clean carbide surfaces.

Keywords: Carbide formation; Carbon film growth; Interface formation; Molybdenum

1. Introduction

The nature of the interfacial region that is formed between thin films and the respective substrate materials is of central importance for the application of these films. In the case of diamond and other carbonaceous films the formation of a carbidic interface is often the primary reaction in the film growth process [1,2]. Structure and composition of the interfacial region can influence important film properties, e.g. crystallite orientation [3] and the nucleation process in the case of diamond, or the adhesion between film and substrate [4,5]. Among the numerous substrate materials employed in thin film deposition the refractory metals form an important group; examples are the coating of medical implants or cutting tools. The refractory metals are, at the same time, known to form stable carbides, which are by themselves of considerable industrial importance because of their exceptional bulk properties such as hardness, high melting point and electrical conductivity [6–8]. The need to gain a better understanding of the interface formation itself emerged during investigations of the bias-enhanced nucleation on silicon and molybdenum [9,10], which preceded the present study.

The interface formation is, on the one hand, determined by the nature of the substrate material, such as diffusion constants and solubility of carbon in the metal and the metal carbide, the enthalpy of carbide formation, and interface energies. On the other hand, the parameters chosen for the respective film deposition are likewise decisive: irradiation of the substrate with energetic ions or the presence of etchants, such as atomic hydrogen [10], can yield substantially different interfaces. The influence of those parameters tied to the respective deposition method is minimized if a low energy carbon beam is used, which can be supplied through electron beam evaporation of graphite. The changes a surface undergoes during the interface formation and early

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0925-9635/99/$ – see front matter
PII: S0925-9635(98)00429-4

stages of film growth can best be observed if surface-sensitive methods are employed. Photoelectron spectroscopy, which is also used in the present study, has already been successfully applied to study the interface formation for different carbon–substrate combinations [2,4,11].

In the study presented here we describe the formation of the interface between molybdenum and amorphous carbon in the absence of hydrogen. The development of the carbide interface is recorded using ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS), which yields information on the chemical composition and the electronic structure of the interface components. In the course of the deposition an Mo_2C surface is produced, which allows us to study the valence band (VB) structure of this carbide phase.

2. Experimental

The carbon was supplied by electron beam evaporation of graphite using an electron beam evaporation source (Omicron, EFM3). The deposition rate was adjusted between 0.3 and 0.5 ML min^{-1} (1 ML = 0.2 nm) and monitored by a quartz crystal monitor. The substrate material was polycrystalline molybdenum, which was subjected to repeated sputter–annealing cycles to minimize the residual oxygen contamination. During the carbon deposition the substrate temperature was held at 400 °C and the sample was subsequently transferred to the analysis chamber without breaking the vacuum. The pressure was kept below 5×10^{-9} mbar throughout the entire deposition and analysis cycles.

The photoelectron spectroscopy analysis was performed on a Leybold EA11/100MCD ESCA system. Mg Kα ($h\nu = 1253.6$ eV) radiation was used to record the core-level spectra (XPS), and a helium gas discharge lamp emitting light in the ultraviolet region (He I, $h\nu = 21.22$ eV) was employed to determine the VB-spectra (UPS). The typical resolution was 0.1–0.2 eV for UPS and 0.9 eV for the XPS measurements. The spectra have been recorded using a constant retardation ratio for the UPS and a constant pass energy for the XPS measurements and are presented here without background or satellite subtraction. The energies of the spectral features discussed are given with respect to the Fermi level E_F and the Au $4f_{7/2}$ core-level line (83.8 eV binding energy) of a clean gold sample.

3. Results and discussion

The VB- and core-level-spectra of the carbon 1s (C 1s) core level, which were recorded for increasing carbon coverage, are shown in Figs. 1 and 2 respectively. The bottommost VB-spectrum in Fig. 1 corresponds to the molybdenum substrate. It exhibits a high density of states at the Fermi edge, two peaks at 1.8 and 4.1 eV binding energy and a weaker peak located around 6 eV. The two peaks at lower binding energy can be assigned to the VB-spectrum of pure Mo, which is dominated by emission of d-electrons due to their larger photoexcitation cross-section at this excitation energy compared with the s-electrons [12,13]. The peak around 6 eV binding energy is attributable to the residual oxygen contamination (about 2.5%) [14]. With increasing carbon coverage the peak located at 1.8 eV gradually diminishes in intensity, and the one originally positioned at 4.1 eV is shifted to higher binding energies up to a maximum of 4.5 eV at a coverage of 3.4 ML.

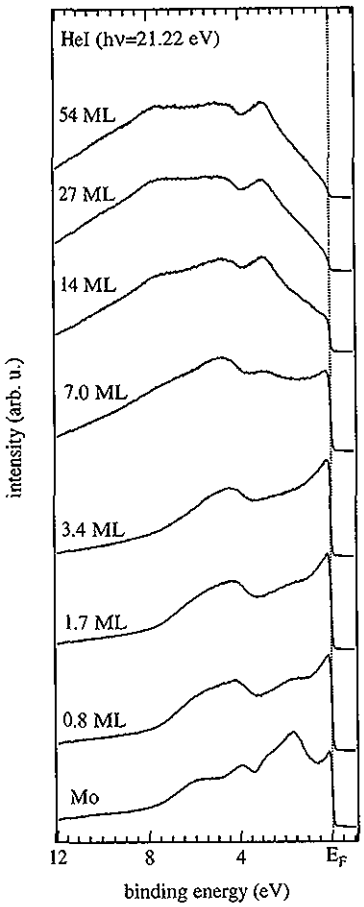

Fig. 1. Evolution of the VB-spectra obtained with He I radiation for increasing carbon coverage.

Beyond a coverage of 3.4 eV a considerable increase in intensity on the high binding energy side above 4.5 eV is observed. This is accompanied by a decrease in the density of states at the Fermi edge and a filling of the valley between the Fermi edge and the 4.5 eV peak. The VB-band spectra now continuously evolve toward the spectrum of an amorphous carbon film which already possesses a partially graphitic structure, as evidenced by the emerging peaks around 3.0, 5.0 and 8.0 eV. A

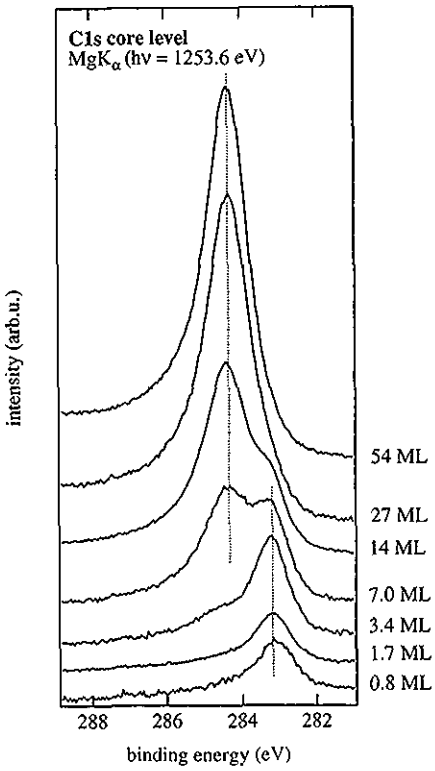

Fig. 2. The C 1s core-level peak as a function of carbon coverage. The bottommost spectrum corresponds to the first carbon deposition step.

comparison with thick amorphous carbon films, deposited at the same substrate temperature [15], confirms the structural similarity to the film obtained here.

Fig. 2 shows the corresponding C 1s spectra. For coverages below 3.4 ML a single peak located at 283.2 eV is observed, which can be attributed to molybdenum carbide [8]. At 3.4 ML an additional component begins to evolve that gains in intensity with increasing carbon coverage. This component is located at a binding energy of 284.3 eV and originates from a pure carbon film. To determine the contribution of both components to the C 1s peak, a fit procedure using Doniach–Sunic functions [16] was applied and the result is summarized in Fig. 3. An equivalent deposition series was performed at a substrate temperature of 600 °C. At this temperature the appearance of a pure carbon phase is only observed for carbon coverages exceeding about 15 ML, which illustrates the strong temperature dependence of the interface formation process. The chemical shift of the Mo $3d_{5/2}$ core level is about 0.2 eV between the pure metal (227.9 eV) and the carbide (228.1 eV) [8,17]. Although this prohibits a reliable fit of the peaks, the change in the position of the Mo $3d_{5/2}$ peak allows one to monitor the progression from the pure metal to the carbidic phase in the course of carbon deposition (Fig. 4).

At 3.4 ML carbon coverage the concentration of carbon amounts to 34%, which is the mean concentration throughout the sample volume accessible by the XPS analysis, and corresponds approximately to the stoichiometry of Mo_2C (the stable carbide phase at this temperature according to the phase diagram [7]). Since carbon is transported into the bulk through diffusion, a concentration profile develops which exhibits a higher carbon concentration close to the surface and a somewhat lower carbon concentration deeper in the bulk. This is in agreement with our observation that, at 3.4 ML, a thin carbon layer has begun to form, whereas the Mo $3d_{5/2}$ peak has not yet reached its final value of 228.1 eV. It is reasonable to assume that the surface itself is dominated by the stable molybdenum carbide, namely Mo_2C.

Turning our attention back to the UPS spectra, we can now interpret the evolution of the VB-spectra before

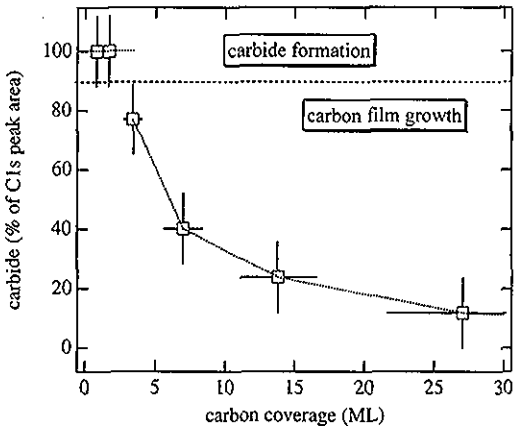

Fig. 3. Contribution of the carbide peak to the C 1s core level. The respective contributions are extracted from the C 1s peak by applying a fit procedure using Doniach–Sunic functions.

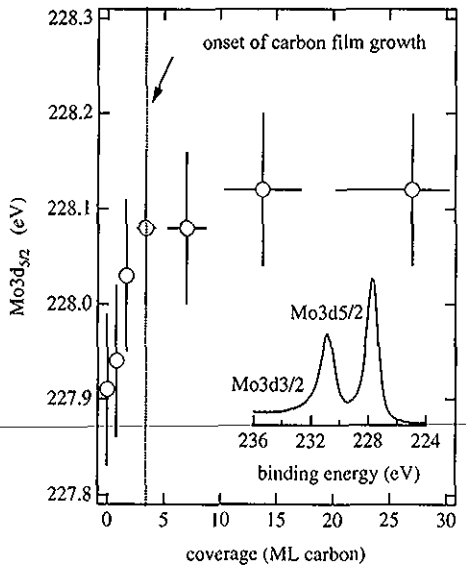

Fig. 4. Position of the Mo $3d_{5/2}$ peak as a function of carbon coverage. The inset shows the Mo 3d peak for the molybdenum substrate prior to carbon deposition.

the carbon film formation as the transition from molybdenum to molybdenum carbide. The VB-spectra at 1.7 and 3.4 ML carbon coverages are dominated by Mo_2C and, therefore, represent the VB of this material. Identical spectra are observed for the deposition series performed at a substrate temperature of 600 °C just before the onset of carbon film formation. In general, the transition-metal carbide band structures are dominated by three bands [14,18]: a metal band formed by the d-electrons and small admixtures of the C 2p states, a lower lying band consisting of the C 2p electrons with contributions from the metal d,p-band, and a low-energy band formed mainly of the C 2s electrons, which has a very small excitation cross-section in the UPS. The metal–carbon bonds dominate the carbide structure, whereas the interaction between the carbon atoms is only weak [7]. Band structure calculations agree according to Gubanov et al. [18] (although they only refer to the band structure without actually showing it) that this general valence structure is applicable to Mo_2C [18], but experimentally determined VB-spectra are, to our knowledge, presented here for the first time. In accordance with this general description of the VB structure, we tentatively suggest the following assignment of the peaks observed in the experimental VB-spectra (Fig. 1): the peak which coincides with the Fermi edge is attributed to those states dominated by the metal 4d band, and the peak at 4.5 eV is associated with the hybrid band, containing contributions from both the metal and the C 2p electrons.

The deposition process can be subdivided into two distinctly different regimes: firstly, the formation of the carbide interface, and secondly, the film growth itself (see Figs. 1 and 2). Only if the carbon flux into the substrate exceeds the incoming flux of carbon atoms is the growth of a carbon film on the surface possible. The bias-enhanced nucleation process of diamond on molybdenum substrates [9] required, for example, much higher initial methane concentrations in the gas phase than used for other substrate materials. The fulfilment of the 'flux condition' depends on the respective carbon loss mechanism in the substrate material. In the case of molybdenum, the solubility of carbon is rather low [19], and the formation of a carbidic layer is therefore strongly favoured. The constant peak position of the carbidic C 1s contribution (Fig. 2) attests to the presence of only one dominant carbon bonding state, namely the carbide. The enhanced diffusivity at higher temperatures leads to a delayed carbon film formation, which can clearly be seen in the comparison of the deposition experiments at 400 and 600 °C: at 600 °C a fivefold increased amount of carbon is required to reach the beginning of surface film growth.

Evidence that the interface growth is not terminated at the onset of carbon film growth is the continued shift of the Mo $3d_{5/2}$ peak position for carbon coverages exceeding 3.4 ML (400 °C), where the appearance of a carbon phase is first observed. This shift of the Mo $3d_{5/2}$ peak illustrates that the thickness of the carbide layer is still increasing, until it exceeds the information depth of the XPS analysis and a constant peak position is observed. The assumption that the interface formation is terminated with the onset of carbon film growth is not applicable in the case of molybdenum: diffusion through the carbide interface is still present and a dynamic rather than static interfacial layer exists.

A rough estimate can be made concerning the thickness of the carbide layer: taking into account the density of the participating phases (Mo, 10.28 g cm^{-3}; C, 2.2 g cm^{-3}; Mo_2C, 9.18 g cm^{-3}), 3.4 ML of carbon yield about 10 ML or 25 Å of the carbide, about one-third of the information depth of the XPS analysis. Around 10 to 15 ML of carbon is then required to push the interface thickness beyond the reach of the XPS analysis. This corresponds rather well to the coverage where the Mo 3d peak reaches a constant peak position.

We have now illustrated one of the limiting cases of interface formation, where the nature of the substrate material dominates the processes that govern the carbide formation. The influence of other deposition parameters, such as ion irradiation or hydrogen etching, can now selectively be studied, thus developing a more thorough understanding of the processes involved. Carbon diffusion in the metal and carbide is certainly one of the driving forces in interface formation; this depends not only on the temperature, but also on the respective carbon and defect concentrations and other properties of the material. This severely complicates the modelling of the interface formation. However, experiments of the type illustrated here can form a basis for such a model in the future. Apart from providing knowledge on the interface formation, it is possible to achieve practically contamination-free carbide surfaces, which allows one to study their electronic structure.

4. Conclusions

We have presented an investigation of the interface formation between amorphous carbon films and molybdenum at elevated substrate temperatures. In a first reaction step the formation of a carbide with Mo_2C stoichiometry is observed. Continued deposition of carbon leads to the formation of an amorphous carbon film, and the amount of carbon required to achieve film growth is strongly temperature dependent. Prior to the onset of carbon film growth a clean Mo_2C surface is observed, which allows one to determine the VB-structure of this carbide. The interface, however, continues to grow in thickness even after the onset of carbon film growth. Diffusion processes through the metal and carbide appear to dominate the interface

formation. Future experiments will allow us to extend this experiment to yield an improved understanding of the influence of different parameters, such as ion irradiation or etchants.

References

[1] R. Haubner, A. Lindlbauer, B. Lux, Diam. Relat. Mater. 2 (1993) 1505.
[2] P. Oelhafen, D. Ugolini, S. Schelz, J. Eitle, Diamond and Diamond-Like Films and Coatings, NATO–ASI vol. 266, Plenum Press, New York, 1992.
[3] E. Maillard-Schaller, O.M. Küttel, L. Schlapbach, Phys. Status Solidi 153 (1996) 415.
[4] S. Schelz, P. Oelhafen, Surf. Sci. 279 (1992) 137.
[5] S. Schelz, P. Reinke, P. Oelhafen, Surf. Sci. 293 (1993) 275.
[6] P.-O. Joffreau, R. Haubner, B. Lux, J. Ref. Hard Met. December (1988) 186.
[7] L.E. Toth, Transition Metal Carbides and Nitrides, vol. 7, Academic Press, New York, 1971.
[8] S.P. Perry, G.A. Somorjai, J. Vac. Sci. Technol. A 12 (1994) 1513.
[9] P. Reinke, P. Oelhafen, J. Appl. Phys., in press.
[10] P. Reinke, P. Oelhafen, Phys. Rev. B 56 (1997) 2183.
[11] D.N. Belton, S.J. Schmieg, J. Vac. Sci. Technol. A 8 (1990) 2353.
[12] J.-J. Yeh, I. Lindau, At. Data Nucl. Tables 32 (1985) 1.
[13] R.C. Cinti, E.A. Khoury, B.K. Chakraverty, N.E. Christensen, Phys. Rev. B 14 (1976) 3296.
[14] A.L. Ivanovsky, D.L. Novikov, V.A. Gubanov, Phys. Status Solidi 141 (1987) 9.
[15] S. Schelz, P. Kania, P. Oelhafen, H.-J. Güntherodt, T. Richmond, Surf. Sci. 359 (1995) 227.
[16] S. Doniach, M. Sunjic, J. Phys. C: Solid State Phys. 3 (1970) 285.
[17] R. Nyholm, N. Mårtensson, J. Phys. C: Solid State Phys. 13 (1980) L279.
[18] V.A. Gubanov, A.L. Ivanovsky, V.P. Zhukov, Electronic Structure of Refractory Carbides and Nitrides, University Press, Cambridge, 1994.
[19] E. Gebhardt, E. Fromm, U. Roy, Z. Metallkd. 57 (1966) 732.