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Tribological performance of polycrystalline tantalum-carbide-incorporated diamond films on silicon substrates

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A B S T R A C T

Polycrystalline tantalum-carbide-incorporated diamond coatings have been made on unpolished side of Si (100) wafer by hot filament chemical vapor deposition process. Morphology of the coatings has been found to vary from (111) triangular-facetted to predominantly (111) square-faceted by increasing the concentration of tantalum carbide. The results have been compared to those of a diamond reference coating with no tantalum content. An increase in roughness has been observed with the increase of tantalum carbide (TaC) due to change in morphology of the diamond films. It is noticed that roughness of the coatings increases as grains become more square-faceted. It is found that diamond coatings involving tantalum carbide are not as resistant as diamond films with no TaC content and the coefficient of friction for such coatings with microcrystalline grains can be manipulated to 0·33 under high vacuum of 10^{-7} Torr. Such a low friction coefficient value enhances tribological behavior of unpolished Si substrates and can possibly be used in sliding applications.

1. Introduction

Since the first successful occurrence of chemical vapor deposition (CVD) diamond synthesis, a lot of research work has been performed to make suitable use of its outstanding physical, mechanical and wear resistant properties. Friction which provides resistance against motion of two objects in contact, and phenomena associated with wear are two key problems in mechanical engineering industry [1]. Diamond being the hardest material, quite inert to most chemical products and good heat conductor possesses a set of such good properties for its tribological applications. However, surfaces of polycrystalline diamond films are usually very rough based on different sizes and orientations of grains that depend on deposition conditions. These factors significantly influence the tribological characteristics of diamond films [1–6]. Moreover, because of hardness and wear resistance properties, transition metal (TM) doped diamonds are much useful for industrial applications as hard shielding. Titanium nitride is among such hard coatings but its behavior is not satisfactory in applications involving low friction [7,8]. Metal carbides such as tungsten carbide being low friction coating of industrial components can overcome this problem [9]. Doping of diamond is an essential feature in terms of tribology and bio-functionality. Boron is one of most widely utilized dopant in this regards. Liang et al. [10] studied the tribological properties for both undoped and boron-doped NCD films and found for diamond/diamond sliding, coefficient of friction decreases with increasing normal loads. They also noticed that the wear rate of boron-doped NCD films is about 10 times higher than that of undoped films. Wang et al. [11] investigated boron doped, undoped microcrystalline and fine grained composite diamond (BD-UM-FGCD) films and noticed that these films perform very small friction coefficient and great friction behavior owing to their high surface smoothness, and also possess excellent wear resistance because of the relatively high hardness of the surface FGCD film and the extremely high hardness of the middle UMCD film. The tribological properties of boron-doped (B-doped), silicon-doped (Si-doped) diamond films were examined by using a ball-on-plate type rotating tribometer [12] and observed that the Si-doped diamond films present the lowest friction coefficient and wear

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rate among all tested diamond films because of their diamond grain refinement effects. However, B-doped diamond films exhibited larger grain size and rougher surface but lower friction coefficient than that of undoped ones. In addition boron doped diamond is found to be highly biocompatible and integrates well with neural tissues, muscles and bones [13]. Boron doped diamond provides support to human neuronal cultures, even when cells have to face an oxidative insult [14]. Moreover, Panda et al. [15] studied the effect of N+ ion implantation on the tribological properties of nanocrystalline diamond (NCD) films and found that these films exhibit superhydrophobic properties and ultralow friction coefficient as compared to undoped films. Such a low friction coefficient was noticed due to the formation of carbonaceous transfer layer on the ball counter body. High friction coefficient obtained in nanotribo-test was caused by severe deformation of ball due to the absence of stable transfer layer. Friction coefficient model can be described by microstructure, phase fraction of sp^2/sp^3 bonding and surface energy of doped/undoped NCD films. Since friction coefficient is found to be proportional to hardness and elastic modulus of these films so, low friction coefficient of doped NCD films might be associated to the formation of large volume fraction of boundary phases such as nanocrystalline sp^2 and a–C related network. The decrease in friction coefficient in N^+ ion implanted films may be elucidated due to their low surface energy [15].

Doped or alloyed diamond-like carbon (DLC) coatings are important as characterized by incorporating different elements in their structure to realize multifunctionality and improved properties as compared to pure DLC films [16]. Such DLC films have potential applications in many industrial fields, such as in cutting tools and dies, magnetic data storage, micro-electromechanical devices, and solar cells, due to their outstanding properties which include high hardness, low friction coefficient, good anticorrosion properties, smooth surfaces, biocompatibility and optical transparency [17,18]. Important process variables affecting the tribological characteristics of such coating involve adhesion promoter intermediate layer, substrate surface roughness, hydrogen incorporation or hydrogen noninvolvement, and coating deposition parameters (bias voltage, etching, precursor gas, substrate temperature etc.). Other factors that affect tribological characteristics include temperature, sliding speed and load, relative humidity, counter surface, and lubrication media [19]. Additionally by controlling the nature, content and distribution of dopants (B, Si, N, O or F and combinations thereof), tailored synthesis of doped-DLC with properties such as hardness, tribological properties, internal stress, adhesion, electrical conductivity or biocompatibility adapted to a desired value for specific applications can be obtained [16]. The surface morphology, microstructure and distribution patterns of elements in the coating and well-adhesion to the silicon substrate have also impact on tribological properties [20,21]. Furthermore, some TM carbides have shown outstanding performance in some applications, although their hardness is not so high [22–24]. Among these are tantalum carbide and refractory metal carbide which have bulk hardness of ~16.6 GPa [25]. Friction and wear characteristics of polycrystalline diamond and DLC coatings without doping or doping with light elements have been studied so far but no literature is found about the frictional behavior of tantalum/tantalum carbide-incorporated diamond. That is why, present study involves polycrystalline tantalum/tantalum carbide-incorporated diamond coatings on unpolished surface of Si (100) wafers to have well-adhesion to the substrate and manipulates their characteristics by varying tantalum content (by increasing the length of Ta wire) in hot filament CVD system during diamond coating on Si and its effect on tribological behavior under high vacuum.

2. Materials and methods

A conventional hot filament chemical vapor deposition (HFCVD) reactor (at Angstrom Laboratory, Uppsala University, Sweden) was used to deposit tantalum-carbide-incorporated diamond films on Si (100) wafers of 10 cm diameter. Before deposition, substrates were cleaned ultrasonically in ethanol, de-ionized water and in hydrofluoric (HF) for removal of any oxide layer. These substrates were then ultrasonically scratched in acetone having nano-diamond powder (2–5 nm), for the promotion of nucleation. A water cooled Mo holder ($\Phi = 8$ cm) was used to position the substrates. The thermal activation of source gas consisting of hydrogen mixed with 1.0% methane was done by eight parallel tungsten filaments kept at a distance of 5 mm from each other. Precision mass flow controller was used to maintain the gas ratio. Deposition process was performed at 2300 ± 50 °C for 20 h keeping the substrates at 900 ± 10 °C. Filament and substrate temperatures were measured by optical pyrometer and K-type thermocouple, respectively. The deposition time also includes initial half an hour time required to attain the desired temperature and pressure. For tantalum coating, 99.95% pure tantalum wires (tensile strength of 543 N/mm^2) of various lengths (25–100 mm) and 0.5 mm diameter were placed in front of the tungsten filaments and heated up to 2300 ± 50 °C in the reactor chamber for another 20 h. The resulting diamond thin film consisted of tantalum carbide (TaC) layer. A rough estimate of the concentration of Ta incorporated into the diamond films was made through energy dispersive spectroscopy (EDS) as there exists low atomic number elements e.g. carbon and possible overlapping of EDS peaks of Si and Ta. It is noted that an approximately 5.82%–11.83% Ta has been incorporated into the diamond films with increasing length of Ta-wire (results not shown). As-deposited films were studied by SEM (LEO 1550), XRD (D500, Cu K_α, $\lambda = 0.1541$ nm) and Raman spectra (Renishaw 2000, 514.5 nm Ar^+ LASER) at room temperature. Raman curves were studied in back scattering geometry and 10 mW LASER was spotted on film surface in accordance with the suggestions of Filik [26]. For tribological measurements on polycrystalline tantalum-doped diamond coatings, a pin-on-disc tribometer was utilized which determines the coefficient of friction. The pin pressed the disc with a force of 1 N, while disc rotated at 0·10–0·12 m/sec to cover a distance of 0·527 km using a motor placed outside the vacuum system. The whole assembly was placed inside a vacuum better than $133{\cdot}32 \times 10^{-7}$ Pa (10^{-7} Torr). The disc was a $20 \times 20\ mm^2$ Si (100) wafer bare or coated with tantalum-carbide-incorporated diamond on its unpolished side for good adhesion with the substrate.

3. Results and discussion

Surface morphology of the diamond films grown on Si wafer in the absence and presence of tantalum wires in the deposition chamber studied by SEM is shown in Fig. 1. These SEM micrographs illustrate a significant change in the film morphology when tantalum is added in the chamber with methane + hydrogen gas mixture. Surface of the undoped diamond film consists of small sized crystallites depicting predominant (111) triangular facets lying parallel to the substrate plane (Fig. 1a). For diamond fabricated with 25 mm tantalum wire, randomly-oriented crystallites are noticed which do not show well-defined edges but form rounded structures (Fig. 1b). In addition, there is a reasonable increase in grain size with traces of secondary nucleation on the crystallites (Fig. 1b). On further increasing the length of tantalum wires (50 mm), secondary nucleation on crystallites is more profound with only a slight rise in grain size as noticed in Fig. 1c. However, when largest length of tantalum wire (100 mm) was used, large crystallites with clear and sharp grain boundaries were observed, which demonstrate an upward growth with dominant (111) square surface (Fig. 1d). Secondary nucleation in this case was reduced but grain growth was high, consequently the top square edges grew to bigger size (Fig. 1d). It was noted that smaller grains merged into the larger ones resulting in sudden rise of grain size. The reduction of secondary nucleation might be associated with decrease of sp^2 bounded graphitic carbon [27,28]. It is evident that diamond coatings using longer tantalum wire depicted faceted morphology with more microcrystalline features and coatings using smaller tantalum wire demonstrate less or round-faceted crystallites. Roughness of these films also increased systematically as the morphology changed from