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Growth of Ti-C nanocomposite films by reactive high power impulse magnetron sputtering under industrial conditions

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A B S T R A C T

Titanium carbide (TiC) films were deposited employing high power impulse magnetron sputtering (HiPIMS) and direct current magnetron sputtering (DCMS) in an Ar–C_2H_2 atmosphere of various compositions. Analysis of the structural, bonding and compositional characteristics revealed that the deposited films are either TiC and hydrogenated amorphous carbon (a-C:H) nanocomposites, nanocrystalline TiC, or Ti/TiC, depending on the C/Ti ratio. It was found that Ti-C films grown by HiPIMS show a C/Ti ratio of close to 1 for a wide C_2H_2 flow range (4–15 sccm), with free C ranging from 0 to 20%. Thus, films ranging from near stoichiometric single phase TiC to TiC/a-C:H nanocomposites can be synthesized. This was not the case for DCMS, where films grown using similar deposition rates as for HiPIMS formed larger fractions of amorphous C matrix, thus being nanocomposites in the same C_2H_2 (above 4 sccm) flow range. For a C/Ti ratio of 1 the resistivity is low ($4–8\times10^2$ μΩ cm) for the HiPIMS films, and high ($>100\times10^2$ μΩ cm) for the DCMS films. The hardness also shows a big difference with 20–27 and 6–10 GPa for HiPIMS and DCMS grown films, respectively.

1. Introduction

TiC is a binary compound (NaCl crystal structure) that exhibits desirable physical properties, such as high hardness, high melting point, chemical inertness, and high electrical conductivity [1]. In thin film form TiC is deposited employing chemical vapor deposition [2], as well as a variety of plasma assisted physical vapor deposition (PVD) techniques. The latter include cathodic arc evaporation [3–5] and magnetron sputtering, either in non-reactive mode, using a single compound Ti-C target material [6], two elemental targets [7–11], or reactively from a metallic Ti target using a hydrocarbon gas (CH_4, C_2H_2) as source of C [6,7,12]. Another feature of the Ti-C binary system is the incorporation of free C at the TiC grain boundaries forming a tissue phase [13]. While thermodynamics predict this to occur above the C solubility limit (~49 at.% C) [1,14], in physical vapor deposited thin films free C may appear already for as low C contents as ~20 at.% [15]. This C content is below the vacancy limit for phase pure TiC (~35 at.% C), below which Ti/TiC is anticipated. Formation of free C is accompanied by the formation of a nanocomposite microstructure in which nanosized metal carbide grains are embedded in an amorphous C [13] or hydrogenated amorphous C [16,17] (when hydrocarbons are used as reactive gases) matrix, denoted as TiC/a-C and TiC/a-C:H, respectively. The nanocomposite thin films can exhibit high electrical conductivity, high hardness, ductility as well as low friction and wear rate which enable their utilization as e.g. self lubricating, low friction coatings [18,19] and electrical contacts [20]. The mechanical strength, the electrical and tribological properties of the nanocomposite films are determined by the C/Ti ratio, the relative fraction of the a-C(:H) matrix, and the size of the TiC grains [7,18,19,21–23].

It is known that the microstructural characteristics of films grown by PVD techniques are controlled by a variety of process parameters, e.g. the growth temperature, the composition of the gas atmosphere, and the energy transferred from the energetic plasma particles to the film forming species [24]. High power impulse magnetron sputtering (HiPIMS) is a technique which provides large fluxes of energetic ions to the growing film. This is achieved by applying short (typically several 10's of μs) high power density unipolar pulses with a duty cycle of a few % to the sputtering target [25–27]. This mode of operation leads to the generation of dense plasmas with electron densities up to $\sim10^{19}$ m^{-3} [28], several orders of magnitude higher than those in conventional magnetron sputtering techniques, e.g. direct current magnetron sputtering (DCMS) [29,30]. This, in turn, causes ionization of a large fraction of the gas and sputtered atoms [29,31,32] allowing for an intense energetic bombardment of the growing film. This has been shown to lead to the growth of smooth

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and dense elemental [33] and reactively deposited compound films [34–36], and enable control over their phase composition [37–39], microstructure [37,40,41], as well as mechanical [40] and optical [38,39] properties. Furthermore, when employing HiPIMS in a reactive mode for oxide deposition an increased process stability in the transition regime between the metallic and the compound mode has been reported [42–44], allowing for a better control of the incorporation of the reactive gas species and thus of the atomic composition of the growing film. Moreover, the increased plasma density in a HiPIMS discharge can influence the plasma chemistry [45]. This may be relevant, since the plasma itself is a carbon source in reactive C_2H_2 processes [46,47].

It is therefore evident that in comparison to conventional magnetron sputtering processes, the HiPIMS process exhibits enhanced capabilities for controlling plasma conditions and the microstructure, composition, and the properties of reactively sputtered compound films. This potential for metal carbide nanocomposite films in general, and TiC/a-C(:H) in particular, remains to be demonstrated.

The present study explores the feasibility of reactive HiPIMS for the growth of TiC/a-C:H thin films, a previously well studied material system of technological relevance to applications, and its implications for the film properties. Ti-C thin films are deposited employing HiPIMS, as well as DCMS for reference, in a reactive Ar–C_2H_2 atmosphere of various compositions. The chemical bonding, atomic composition, and the microstructure of the films at the various deposition conditions are investigated and correlated with their mechanical and electrical properties.

2. Experimental procedures

Depositions were carried out in a commercial Inline Coater 400 (Impact Coatings) type high vacuum system with a base pressure below 6.7×10^{-4} Pa (5×10^{-3} mTorr). The working principle of the deposition system includes sequential, individual processes in isolated, 0.28 m high and 0.4 m in diameter, cylindrical chambers, and is described in detail elsewhere [48]. The experiments were performed employing a rectangular (21 cm × 10 cm) Ti target (purity > 99.3%). The target was mounted on a magnetron cathode which exhibited a magnetic field strength of 350 G at the race track. Films were deposited on Si (100) and ~100 nm SiO_2/Si substrates, which prior to deposition were supersonically cleaned in isopropanol at 70 °C for at least 15 min. No substrate rotation or intentional substrate heating was used during the depositions, while a bias potential of − 150 V was applied on the substrate. Each deposition was preceded by three minutes Ar plasma etching at pressure of 1 Pa (7.5 mTorr) by applying unipolar voltage pulses with an amplitude of 450 V, a pulse width of 1.6 μs, and at a frequency of 250 kHz to remove surface contaminants from the substrates. Films were grown for 15 min at a constant Ar (purity 99.9999%) flow of 30 sccm, resulting in a partial pressure of 1 Pa (7.5 mTorr) while the C_2H_2 (minimum purity 99.6%) flow was varied from 0 to 20 sccm, resulting in slight increases in the total pressure up to 1.1 Pa. The target-to-substrate distance was 12 cm. Power was supplied to the sputtering target by a Sinex 3 (Chemfilt Ionsputtering) generator, capable of operating either in voltage regulated HiPIMS mode, or power regulated DCMS mode. Depositions were performed both in DCMS and HiPIMS modes. The DCMS processes were operated at constant power of 0.6 kW. For the HiPIMS depositions, an average target power of 2 kW was maintained by adjusting the target voltage. The pulse repetition frequency was 400 Hz and the pulse width was approximately 75 μs. The larger average target power used in HiPIMS experiments (as compared to the DCMS ones) was selected in order to obtain equal deposition rates from a metallic target for both techniques. Thus, for similar arrival rates of film forming species, the ion-to-neutral ratio and ion energy, which are different for DCMS and HiPIMS, were the main parameters varied. This experimental strategy was adopted to facilitate a straightforward comparison of the deposition processes and shed light on the fundamental film growth mechanisms. Moreover, a few control experiment films were grown employing DCMS at an average power equal to that used for the HiPIMS depositions. This was done to allow direct comparison of the two deposition methods, as well as to decouple possible effects of the choice of deposition method (i.e. DCMS and HiPIMS) and the average target power applied to the cathode. The deposition sequence of the samples was randomized. Prior to each deposition the target was sputter cleaned in constant current mode for at least 10 min.

The crystal structure of the deposited films was investigated by means of X-ray diffractometry (XRD), performed in a diffractometer equipped with a Cu Kα source operating in both θ–2θ and grazing incidence geometries. Film thicknesses, as well as surface and cross-sectional morphology were obtained from scanning electron microscopy (SEM, LEO 1550 Gemini) operating at 10 keV. The film thickness was measured on fractured specimen cross sections, and averaged for at least five measurements collected from sites spanning the full substrate width. Compositional and chemical analysis was performed by X-ray photoelectron spectroscopy (XPS) using a Physical Electronics Quantum 2000 spectrometer equipped with a monochromatic Al Kα X-ray source. The XPS sensitivity factors were calibrated against a reference sample with a known composition as previously determined by time-of-flight elastic recoil detection analysis (ToF-ERDA) [49]. Owing to the fact that the samples were analyzed during different sessions, and that the XPS equipment may be subject to charge referencing, the binding energies recorded may appear shifted when comparing different analysis sessions. To circumvent this issue, already analyzed samples were re-measured in each session, and comparison allowed accurate deduction of any shifts in binding energy between sessions. The XPS data presented in figures have been shifted according to this procedure. Composition was determined from sputter depth profiles attained using 4 keV Ar^+ ions rastered over a 2 × 2 mm area. High resolution spectra were recorded at an approximate depth of 15 nm after sputtering using 200 eV Ar^+ rastered over a 1 × 1 mm area. In the latter case, low ion energy was used in order to minimize the contribution of sputter damage, in the high resolution spectra; previous studies have shown that no preferential sputtering (i.e. no stoichiometry changes) occurs in this system using 4 keV Ar^+ [50]. The peaks in the recorded spectra were fitted for Shirley background and 20% Lorentzian peak functions. The fitting enabled to calculate the area below each peak. The instrumental error in the XPS measurements and peak fits were both estimated to be 5% or less. To evaluate the amount of H incorporation in the films, selected samples were analyzed using ToF-ERDA using 40 MeV $^{127}I^{9+}$ ions. The ion incidence angle relative to the surface normal was 67.5° and the detector was positioned at a recoil scattering angle of 45°. For evaluation of the ToF-ERDA data the CONTES code was employed [51], and a reference sample with known H content was used for calibration of the data. Electrical properties were evaluated by four point probe measurements on samples grown on the insulating SiO_2/Si substrates, using a Model 280C (Four Dimension) apparatus. The measured sheet resistivity values were multiplied by the respective film thicknesses as assessed by cross sectional SEM measurements to obtain the resistivity. Films grown on the SiO_2 substrates showed no differences to the films grown on Si, as confirmed by XRD and cross section SEM. Nano indentation (Umis 2000) was employed to measure the hardness values. A Berkovich tip was indented a minimum of 10 times at a load of 5 mN, corresponding to indentation depths of ~10–15% of the film thickness, yielding a relative hardness deviation of no more than ~6%. The load was chosen after investigating several indentation loads, thus finding a value causing plastic deformation, while showing marginal influence of surface roughness, and minimizing any influence of the substrate. The hardness was evaluated according to the Oliver–Pharr method [52].