



Reactive processes in the high target utilization sputtering (HiTUS) W-C based coatings



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ABSTRACT

High Target Utilization Sputtering (HiTUS) is a novel technique with an independent plasma source, which offers higher plasma densities, possibilities for the increase of the level of ionization of the sputtered material and significant reduction of negative effects accompanying reactive sputtering related to target poisoning. The aim of the work was to investigate some details of the reactive sputtering behavior during HiTUS and the possibilities of this technology in the increase of the hardness of W-C coatings. It was found out that HiTUS plasma is similar to that in DCMS and hysteresis behavior of sputtering rates during reactive sputtering after modification of acetylene flow was suppressed. The reason seems to be related to higher sputtering rates due to high plasma density from the independent plasma source compared to target poisoning rates within limited acetylene addition range. The reactive HiTUS resulted in substoichiometric amorphous or nanocrystalline WC_{1-x} /amorphous carbon coating containing at least 20% of free disordered carbon. The amount of carbon was proportional to the acetylene flow. Slight shifts of G peak of Raman spectra toward higher values at higher RF bias power were attributed to ordering of carbon structure. Moreover, hardness increased approximately linearly with biasing power within limited acetylene flow range. The highest nanohardness values of HiTUS W-C coatings of around 33 GPa–35 GPa were comparable to those obtained in the best magnetron sputtered coatings which emphasized the applicability of HiTUS technology in hard coatings.

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1. Introduction

The evolution of PVD magnetron sputtering techniques in thin film deposition technologies [1,2] is oriented toward the increase of the sputtering rates, suppression of arcing and thermal loads on the target and substrate [3], better control of the structure, residual stresses, adhesion and resulting mechanical and functional properties of the coatings [3–5]. In the case of reactive sputtering, suppression of the negative effects related to target poisoning is of the main interest [6–8]. The solutions to achieve these requirements are based on the modifications of the magnetic field constraining plasma in the vicinity of the target [1] and in the increase of the degree of ionization of the sputtered material [2,9]. At the end of last millennia, the later approach resulted in the techniques when the sputtered vapor has more ions than neutral atoms and molecules [9] and described by a common term “iPVD” (Ionized Physical Vapor Deposition) [10]. The most recent representative

among the iPVD techniques is the high power impulse magnetron sputtering (HiPIMS) or high power pulsed magnetron sputtering (HPPMS) [2,11]. However in 2009, the first papers reporting the use of new deposition technique based on remote plasma sputtering [12,13] and referred as High Target Utilization Sputtering (HiTUS) appeared [14–16]. In contrast to magnetron sputtering, HiTUS uses an independent plasma source driven by RF power supply separated from the deposition chamber. The Ar plasma is extracted into the chamber by a “launch” electro-magnet. Due to the small plasma energy of Ar ions (~ 10 eV), no sputtering occurs at this stage and plasma is just flooding the chamber. The magnetic field of a “steering” electro-magnet underneath the target transform plasma into a beam directed onto the target. To achieve ion energy necessary for target sputtering, another independent RF power supply is used to bias the target [13–16]. Thus, an independent control of plasma density and sputtering ion energy is possible. This results in the reduced ion bombardment of the substrate and its temperature, higher deposition rates, densities and reduced intrinsic stresses with over 90% utilization of target surface [13–17]. A modification of HiTUS technology has been developed in South Korea under the name “High Density Plasma Assisted Sputtering Source (HiPASS)”

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[18]. The difference is only in the remote plasma source—it uses the hollow cathode discharge gun with DC power instead of RF plasma source.

HiTUS is suitable for the deposition of single phase as well as multicomponent coatings and reactive sputtering. It has been successfully used for the deposition of oxide coatings for optical and other functional applications, e.g., indium tin oxide (ITO) [14,19], high dielectric constant HfO_x [20] and oriented ZnO films [21], nitrides including antireflective AlN coatings [16] and amorphous Si_3N_4 [22], and even for IrMn/Co-2FeSi Heusler alloys [23]. HiPASS has been applied TiN coatings and under optimized conditions, hardness of TiN coatings approached 48 GPa [24]. It is considerably higher than in the case of conventional magnetron sputtering. Despite such clear demonstration of significant potential of remote plasma source sputtering technique in the field of hard coatings, the use of HiTUS and HiPASS to other hard coating systems for engineering applications is very limited. Only few conference papers have been published on W-C coatings prepared by HiTUS up to now [25–27]. Although they showed better mechanical properties compared to those deposited by HiPIMS, more detail investigations of the parameters controlling the structure and resulting properties are still missing.

W-C based coatings are a part of metal doped diamond-like carbon coatings covering wide range of properties depending on their composition and techniques of deposition. The hardness up to 40 GPa has been obtained in the case of dual DC magnetron sputtered W-C coatings composed for solid solution of carbon dissolved in tungsten. When the content of free carbon increased, coating hardness gradually decreased to <10 GPa [28]. It corresponded to gradual phase changes—higher C contents resulted in the formation of W_2C and then to WC_{1-x} and WC_{1-x} /free C coatings. Because of free soft graphitic carbon acting as a lubricant, the coefficient of friction (COF) exhibited opposite behavior—it was ~0.8 in low C content W-C coatings and decreased to ~0.1 when the amount of free C exceeded 50% [28,29]. Although W-C coatings are usually prepared by conventional DC and/or RF magnetron sputtering [28,29], the first attempts to use HiPIMS and even HiTUS have already been reported [25–27]. The hardness of the HiPIMS made W-C coatings was only around ~20 GPa and the coefficients of friction were 0.2–0.3 within the range of the studied parameters whereas that of HiTUS coatings was up to 34 GPa and coefficient of friction around 0.35–0.45. The obtained maximum hardness values were slightly lower than the maximum hardness of 43 GPa obtained on the basal planes in WC single crystal grains [30]. Thus, further improvement of the hardness of W-C coatings can be theoretically expected even without the contribution of nanocomposite structure. Therefore, the aim of the work is to investigate the possibilities of HiTUS technology in further increase of the hardness of W-C coatings.

2. Experimental procedure

The studied W-C coatings were deposited using High Target Utilisation Sputtering system S 500 (Plasma Quest Ltd., United Kingdom). It consists of a remote plasma source with an independent RF power source connected to a deposition chamber with target holder for up to four targets with the diameter up to 1016 cm (4 inch) driven by RF power supply and RF power biased rotating specimen holder for the targets. The system enables reactive processes using 3 different gases (N_2 , H_2 , C_2H_2) besides Ar and it also contains residual gas analyser (HPQ3, MKS), film thickness monitor, pyrometer and optical emission spectrometer (AvaSpec 2048, Avantes).

The studied coatings were deposited on the polished heat treated bearing steel (STN 14109) (diameter ~25 mm, thickness ~3 mm) and sometimes simultaneously on Si (30 mm × 30 mm) wafer or microslide glass substrates. After preliminary *in-*

situ plasma cleaning using 200 W RF power for 10 min, thin (50–100 nm) Si or Ti bond layer has been deposited on the substrate to improve adhesion of the subsequent coating. The deposition occurred from the target of stoichiometric WC with the diameter of 762 mm (3 inch), using constant values of the following parameters: RF power on remote plasma source ~2.5 kW, RF power on the target ~0.5 kW, distance between the target and substrate ~18 cm and deposition time ~1.3 h. The resulting coating thicknesses at those conditions varied around 1 μm depending of the other deposition condition. The variables included working pressure which was controlled by Ar flow (60–180 sccm) within the range 0.4–1.2 Pa, flow of C_2H_2 added in the working atmosphere (within the range 0–10 sccm) and RF power (bias) on the substrate within the range 0–100 W. The deposition rates were monitored continuously during the process using quartz film thickness monitor (FTM) located close to the substrate. However, they refer to sputtering rates rather than to deposition rates because no bias can be applied to FTM. Possible coating density changes due to acetylene additions on the measured rates were omitted.

The structure and composition of the studied coatings have been observed by FESEM/FIB (Auriga Compact, Zeiss) with EDS system Raman microscope (XploRA, Horiba Yvon Jobin) using 532 nm laser and X-ray photoelectron spectroscopy (XPS; Omicron multiprobe with hemispherical analyser). The analysis has been performed by monochromatic Al $K\alpha$ X-rays (1486.6 eV) and using carbon C1s line (for hydrocarbon, binding energy 284.8 eV) to calibrate the binding-energy scale. The spectra have been measured at 45° with 10 meV steps and 20 eV pass energy at ambient temperature. The surface contamination has been removed by sputtering with 2 keV Ar ion energy. The thickness of the coatings was measured by confocal microscope/optical interferometer (Neox Plu, Sensofar, Spain) at the sharp edge and by FESEM on the fractured surfaces. The composition depth profiles were obtained from GDOES measurements (GD Profiler 2, Horiba Yvon Jobin). Phase composition was investigated by an X-ray diffraction (X'pert Pro, Panalytical). The instrumented hardness of the coatings was measured on nanoindenter (G200, Agilent) in CSM (sinusoidal) loading mode with constant strain rate (0.05 s^{-1}) on a matrix of 25 indents. The resulting hardness of each coating was determined from the maximum of the corresponding hardness depth profile averaged from at least 20 indents and considering “10% depth rule”.

3. Results

3.1. HiTUS plasma conditions and reactive sputtering

The conditions in plasma during HiTUS have been investigated by means of the optical emission spectroscopy to determine the differences compared to those during conventional DC magnetron sputtering (DCMS). Fig. 1a illustrates general view on the spectra (the intensities were not normalized) in DCMS and HiTUS plasmas in a wide range from 200 nm up to 1000 nm. The spectra are very similar with the absolutely dominant peaks of Ar^0 in the range 650–850 nm. The peaks corresponding to ions Ar^+ were present only in the wavelength range below ~500 nm. They were identified both in DCMS and HiTUS and the difference seemed to be only in the relative ratio of Ar^+ peaks at 506 nm and 484 nm. The peaks corresponding to the other ions are shown in Fig. 1b in the case when C_2H_2 has been added into Ar atmosphere. Because of limited resolution of the spectrometer (fixed 0.6 nm wavelength step), only the most intensive peaks of Ar^+ and W^0 could be identified. The obvious differences between HiTUS and DCMS was in the intensity of Ar^+ peaks in the range 434.9–480.7 nm, which were significantly enhanced in HiTUS compared to DCMS. Note the presence of CH^0 due to acetylene addition.

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