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Growth and characterization of chromium carbide films deposited by high rate reactive magnetron sputtering for electrical contact applications

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ABSTRACT

Chromium carbide films with different phase contents were deposited at 126 ± 26 °C by industrial high rate reactive magnetron sputtering, using both direct current magnetron sputtering (DCMS) and high power impulse magnetron sputtering (HiPIMS). Film structure and properties were studied by SEM, XRD, TEM, XPS, NRA, Raman spectroscopy, nanoindentation, unlubricated reciprocating sliding experiments, and a laboratory setup to measure electrical contact resistance. The films consisted of amorphous a-CrC_y, a nanocrystalline minority phase of metastable cubic nc-CrC_x, and a hydrogenated graphite-like amorphous carbon matrix (a-C:H). The DCMS and HiPIMS processes yielded films with similar phase contents and microstructures, as well as similar functional properties. Low elastic modulus, down to 66 GPa, indicated good wear properties via a hardness/elastic modulus (H/E) ratio of 0.087. Unlubricated steady-state friction coefficients down to 0.13 were obtained for films with 69 at.% carbon, while the electrical contact resistance could be reduced by two orders of magnitude by addition of a-C:H phase to purely carbidic films. The present films are promising candidates for sliding electrical contact applications.

1. Introduction

Sliding electrical contacts play an important part in everyday life. Most materials used today are expensive noble metals or alloys, like Au, Pd, and Au–Co, which are applied as thin films on a conductive substrate. More cost-effective alternatives are base metals and alloys, such as Ti and stainless steel, but they more easily form high resistance surface oxides [1], requiring high contact forces to break through. Such forces cause severe wear and are unsuitable in e.g. consumer electronics. This can be improved by using soft metals, such as Ag, but they will exhibit severe wear even at low contact force [2], leading to reduced reliability and shortened product life. A thicker film, adding to the product cost, is then required to compensate for the loss of metal. Thus, there is a driving force to design new films with lower cost and improved material properties.

Replacing noble metals with nanocomposite transition metal carbide/amorphous carbon (Me–C/a-C) films, with nanocrystalline carbide grains embedded in an amorphous carbon matrix, is a proposed alternative [3]. The carbon matrix adds a polymeric-like character with high hardness/elastic modulus ratio and low surface energy [4], providing reduced friction and improved wear properties by the formation of graphite-like tribofilms. Meanwhile, the carbide phase retains its high hardness, low resistivity, and high corrosion resistance.

Several studies on various carbide-based nanocomposites, e.g. Ti–C [5], Ti–Ni–C [6], Ti–Si–C [7], Ti–(Si, Ge, Sn)–C–Ag [8,9], Ti–Si–C–Ag–Pd [10], and Nb–C [11], have demonstrated promising properties and potential use in electrical contact applications. However, the Cr–C system has some unique properties which are interesting for a new contact material. Perhaps the most striking property is that Cr–C has a high glass forming ability and a wide glass forming range compared to other Me–C systems [12], meaning that an amorphous structure can be obtained over a wide range of experimental conditions and film compositions. This behavior makes it possible to co-sputter nanocomposite a-CrC_y/a-C films with separate phases of amorphous carbide and amorphous carbon, making the films soft yet reasonably conductive [13,14]. It is also possible to sputter nanocrystalline nanocomposites [15–17], and this microstructural window offers great potential to tailor the functional film properties. Some studies have reported high hardness and very low electrical resistivity for Cr-rich Cr–C films [15,18,19],

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although in a sliding contact application such films are unlikely to perform well due to high coefficients of friction [20]. A nanocomposite structure, on the other hand, notably reduces friction and improves wear properties [16,20–22]. Moreover, Cr–C/a-C films were recently shown to be protected from deep oxidation by an extremely thin Cr oxide film, where the a-C phase reduced surface concentrations of oxidized Cr by nearly 50% [17]. However, no one has studied Cr–C/a-C films for the purpose of electrical contact applications.

The aim of this study is to investigate the structural, mechanical, tribological, and electrical contact properties of Cr–C films deposited by high rate reactive magnetron sputtering at low substrate temperature. Although direct current magnetron sputtering (DCMS) offers high deposition rates, the method can lead to low-density films with hampered functional properties. Therefore, films grown by high power impulse magnetron sputtering (HiPIMS) were also studied. HiPIMS provides a higher degree of ions in the deposition flux, which can lead to denser films with smoother surface and better functional properties, however at the cost of reduced deposition rate [23]. In this study, the two sputtering methods, different reactive gas flows, and two substrate bias potentials were used to deposit Cr–C films with different compositions. Relationships between deposition conditions, composition, structure, chemical bonding, and functional properties are established.

2. Experimental details

Cr–C films were deposited using an InlineCoater™ 500 (Impact Coatings AB, Sweden), which is an industrial short-cycle high vacuum physical vapor deposition system (details are given elsewhere [24]). The base pressure was 1.3×10^{-4} Pa. One unbalanced magnetron was mounted on the second process chamber for single-sided top-down deposition geometry with a perpendicular target-to-substrate distance of 15 cm. The sputtering target consisted of industrial grade Cr (rectangular 898 cm^2, purity at least 99.7 at.% Cr). All depositions were made by DCMS or HiPIMS. In the case of DCMS, the electric current density was 0.022 A cm^{-2} and the target potential was 450–550 V. In the case of HiPIMS, the peak electric current density was 0.40–0.50 A cm^{-2}, the target potential was adjusted to yield an average power of 5 kW, the pulse frequency was 500 Hz, and the pulse width was 100 µs. The target was pre-sputtered for 3 min prior to each experiment. Metallic operation was confirmed by stable plasma emission intensity from a Cr line and by stable electrical potential (500 V) of the magnetron in constant current mode (20 A). Substrates of Si and SS316L polished to a mirror-like surface finish were placed flat down on a Cr-coated stainless steel fixture with a mass of 10 kg. The starting temperature of the fixture was 126 ± 26 °C for each batch, and process-induced heat increased the temperature during deposition to 148 ± 18 °C. Film deposition was preceded by Ar plasma etching for 2 min at 1.9 Pa by applying unipolar potential pulses with an amplitude of −700 V, a frequency of 250 kHz, and a pulse width of 1.6 µs. A thin Cr layer (80–100 nm) was deposited at 1.1 Pa to improve adhesion and to deposit the carbide films on chemically similar surfaces. Different C_2H_2 gas flow rates (0–78 sccm) were used to control film composition. Typical reactive process pressure was 1.1–1.5 Pa. Process time was adjusted to obtain a similar film thickness (1.29 ± 0.18 µm). A constant substrate bias potential (U_b) of −50 V was normally applied. Some films were deposited at $U_b = -150$ V in order to more strongly differentiate the DCMS and HiPIMS processes.

Film microstructure was studied by grazing incidence X-ray diffraction (GIXRD), using a diffractometer equipped with a Cu $K\alpha$ radiation source and parallel beam geometry, and transmission electron microscopy (TEM), using a FEI Tecnai G^2 TF 20 UT microscope operated at 200 kV. Cross-sectional TEM samples were prepared using a Zeiss ES-1540 Crossbeam FIB using Ga-ions with the so-called lift-out technique [25]. Film cross-sections and surfaces were studied using a Leo 1550 field emission scanning electron microscope (SEM) with an electron gun potential of 10 kV. Film composition and chemical binding energies were determined by X-ray photoelectron spectroscopy (XPS), using a PHI Quantum 2000 spectrometer with monochromatic Al $K\alpha$ radiation. XPS sensitivity factors were calibrated by elastic recoil detection analysis of reference samples and the measurement accuracy for this method is typically a few atomic percent. High resolution C1s, Cr2p and O1s spectra with a step size of 0.05 eV were obtained using a pass energy of 11.75 eV. Pre-sputtering was performed to depths of both ~8 and ~15 nm at different film spots, using 0.2 keV Ar^+ for 75 min and 0.5 keV Ar^+ for 20 min, respectively, to remove surface contamination. The Ar^+ ion incidence angle was 45°. There was no significant difference in composition between the two measurements. The average composition of each film is reported with a precision of ±2 at.%. Depth profiles obtained using 4 keV Ar^+ resulted in lower carbon contents (4–12 at.%, 95% CI), similar to previous results [17], and were only used to confirm that there was no major deviation in bulk composition. Chemical bonding is reported based on pre-sputtering using 0.2 keV Ar^+ to minimize sputter damages [26]. Hydrogen content was analyzed by nuclear reaction analysis (NRA) using a beam energy of 6.8 MeV to obtain bulk information. Film composition will generally be discussed without the relative contribution of hydrogen. The structure of the carbon phase was studied by Raman spectroscopy, using a Renishaw Micro Raman 2000 spectrometer with a 514.5 nm Ar laser operated at 25 mW.

Friction properties were studied by unlubricated reciprocating experiments in a standard indoor environment (22 °C, RH = 42%) using ball bearing 100Cr6 steel balls with a diameter of 10 mm. The normal load was 5.0 N, the stroke amplitude was 10 mm, and the frequency was 2.0 Hz. Mechanical film properties were studied by nanoindentation, using a CSM Instruments Ultra Nano Indenter XP. The indenting part was a diamond Berkovich tip exerting a maximum load of 1200 µN, which resulted in penetration depths of 60–100 nm. Electrical contact resistance was basically measured in a four-wire setup, using an Au/Ni probe (Ø = 1.2 mm), further described elsewhere [9]. The software was improved to acquire average contact resistance in a steady state, defined as a relative difference in resistance smaller than 3% for a minimum of three consecutive measurements. Contact force was 1.00 ± 0.01 N. At least 3 measurements, in different spots, were made for each film.

3. Results

3.1. Film composition and deposition rates

A series of chromium carbide films with total carbon content ranging from 19 to 69 at.% were deposited. Oxygen content was determined to be 3 at.%, which is an acceptable level for a high vacuum chamber. NRA was only performed for one DCMS and one HiPIMS sample, both with a C/Cr ratio of about 1.3. The hydrogen content in both films was determined to be 1.3 wt.% H, corresponding to an atomic H/C ratio $= 0.68 \approx 2/3$. It is likely, however, that the hydrogen content should vary with carbon content in the film and further studies are required to establish the variation in H/C ratio at different compositions.

The deposition rates for pure Cr (no added C_2H_2 gas) were 480 $\mathrm{nm \cdot min^{-1}}$ and 125 $\mathrm{nm \cdot min^{-1}}$ for the DCMS and HiPIMS processes, respectively. The addition of C_2H_2 gas reduced deposition rates significantly. Typically, deposition rates for films with a carbon content of 20–40 at.% C, or more, were 60% lower than those for pure Cr films. The reduction in deposition rate with addition of C_2H_2 gas to the discharge can be explained by the formation of carbon-containing compounds on the target surface, and these compounds will sputter at a lower rate compared to Cr [27].

The DCMS and HiPIMS processes were carried out at different current densities and in the case of HiPIMS with a pulsing frequency. It is therefore difficult to directly compare the two processes with respect to their conversion efficiency of the C_2H_2 gas. From the gas flow rates and target currents, it is possible to calculate the number of C_2H_2 gas molecules per electric charge which was required to give a certain film composition. The gas flow rate can be expressed as the number of gas molecules per second $\dot{n}$ (s^{-1}) according to Eq. (1), where $\dot{V}$ is the