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Correlation between microstructure and mechanical properties of TiC films produced by vacuum arc deposition and reactive magnetron sputtering.

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Abstract

We have studied the synthesis of TiC films by vacuum arc deposition and reactive magnetron sputtering over a wide range of compositions. The films were deposited on silicon and tool steel. The films were characterized by various techniques: Auger electron and X-ray photoelectron spectroscopies, Rutherford backscattering, transmission electron diffraction and X-ray diffraction. Mechanical properties such as stress, adhesion, friction coefficient and wear resistance were obtained by carrying measurements of the curvature of the silicon substrate, pull tests, and ball-on-disk tests, respectively.

Both techniques successfully produced a broad range of TiC_x film compositions. In both cases, excess carbon is accommodated in interstitial sites in the B1 structure or forms an a-C phase. For high carbon concentrations, the lack of adhesion encountered in the sputtered films was overcome in the vacuum arc films by the high energy of the depositing ions. The major composition difference was the incorporation of hydrogen in the sputtered films. The texture of the films prepared by the two techniques differed. The wear of films with similar Ti:C ratios is comparable despite the difference in film microstructure and structure of the interface.

I. Introduction

Titanium carbide combines the advantages of high melting point (3260 K) and hardness (2200-2700 kgf/mm^2) with those of a relative lightness (density 4.93 x 10^3 kg m^{-3}). It also exhibits high resistance to both corrosion and oxidation and a relatively low friction coefficient. So it is an excellent candidate as a coating for applications in harsh environments.

For the deposition of titanium carbide coatings many methods have been used, among them: chemical vapor deposition [1-3], activated reactive evaporation [4], plasma assisted chemical vapor deposition [5], and physical vapor deposition [6-8]. The authors studied previously the synthesis of TiC_x films by two techniques: reactive magnetron sputtering [10] and vacuum arc

deposition [11], but no comparison between films produced by the different techniques has been performed.

In the present paper, we provide a comparative evaluation of TiC_x films produced by reactive magnetron sputtering and filtered cathodic arc deposition. Film composition, microstructure and wear properties were characterized for films prepared under a variety of process conditions. Because of its importance in wear applications, the adhesion strength between the deposited films and the substrates was also characterized.

II. Experiment

Hydrogen-free TiC_x films were produced by mixing streams of fully ionized Ti and C plasmas produced`by filtered cathodic arcs [12]. Operation of the particular experimental embodiment used in this investigation was carried out in a repetitively pulsed mode, with pulse duration of several milliseconds. The arc current was in the range of 100 to 300 A and the repetition rate was 1 Hz. Both plasma streams were magnetically filtered in order to eliminate the presence of macroparticles in the depositing films. The substrate was negatively pulse-biased with a pulse-on time of 2 μs and time between pulses of 6μs. During the time that the negative voltage was applied to the substrate, the Ti and C ions from the mixed plasma streams were implanted in the growing film. When no bias voltage was applied to the substrate, Ti and C ions were quenched and condensed on the surface of the growing film.

Also, hydrogenated TiC_x films with various thickness and compositions were prepared by direct current reactive sputtering of a 99.9% pure titanium with a commercial planar balanced magnetron apparatus (Leybold LH560) using argon as the working gas and methane as the reactive gas. The source-to-substrate distance was 57 mm and the target was 90 mm in diameter. A more detailed description of the apparatus can be found elsewhere [10]. In all experiments the substrates were kept at ground potential and at room temperature. The experiments were carried out in the dynamic mode; the total pressure was kept constant at 0.35 Pa, corresponding to a total flow rate of 100 sccm (standard cubic centimeters per minute). The substrate surfaces were etched for 120 seconds with argon ions. Before any deposition on the substrate, the target was sputtered in pure argon to clean the surface. The deposition conditions were then established in the chamber and the deposition was carried out on a shutter until steady state conditions were reached. The shutter was then removed to start the deposition on the substrate.

The films were deposited on doped (100) silicon single crystals for structural and composition analysis and on polished 496 oil hardening tool steel for mechanical tests. No attempt was made to remove the native oxide on silicon prior to the introduction in the chambers.

The composition and bonding of the elements in the films were investigated by both Auger electron (AES) and X-ray photoelectron (XPS) spectroscopies. The AES characterizations were performed with a PHI 590 AM and a PHI 660 spectrometers using a primary energy of 3 keV. Ion etching was

used to remove surface contaminants before analysis and to check the in-depth homogeneity of the samples. The XPS analyses were performed in a PHI 5300 apparatus using a magnesium anode and equipped with a small spot analysis lens. The XPS data were deconvoluted to obtain information on the different bonding states of carbon and titanium atoms. The Ti:C ratio was obtained by Rutherford backscattering spectroscopy (RBS).

Morphology and crystallinity of the films were determined by transmission electron microscopy (TEM) carried out in a Topcon 002B microscope with point resolution of 0.19 nm at 200 kV and by X-ray diffraction (XRD) in a SIEMENS 5000 diffractometer with a thin film attachment. The thickness of the films ranged from 80 to 250 nm and was measured by profilometry.

The adhesion between the films and the steel substrates was measured by a pull test. The stress was obtained by measuring the bending radius of the silicon substrates with a dual-wavelength TENCOR FLX 2320 interferometer. The tribological behavior was studied using a CSEM ball-on-disk tester. The measurements were carried out at room temperature in laboratory air with a relative humidity of about 50%. Sapphire balls; 6 mm in diameter were used for these tests. The sliding speed was approximately 0.3 m/s with 382 rotations per minute. The load in all tests was 2 N (initial Hertzian pressure around 0.8 GPa). During testing the friction force was recorded. SEM and optical microscopy were used to study the wear tracks of the disks and the wear scars of the balls.

III. Results and discussion

Composition, bonding and homogeneity

Table 1 shows composition and bonding states of films produced under different deposition process conditions. For sputtered films the current density of the discharge was kept constant at 8 mA/cm^2 and for the vacuum arc deposited films all parameters were kept constant except the C/Ti pulse duration ratio for the films presented in the table. The composition was deduced from the RBS data and the bonding from the XPS and AES data. Despite the use of stoichiometric titanium carbide powder as a standard, it is difficult to establish precisely the stoichiometry of the films from AES and XPS due to strong changes in the peak shapes in the spectra. On the other hand, RBS gives exclusively atomic ratios and no information on the bonding states. It can be seen from Table 1 that a large range of compositions can be produced by the two deposition techniques used in this work.

The XPS and AES results are consistent and show that carbon to carbon bonds and titanium to oxygen bonds coexist with carbon to titanium bonds. The oxygen content in the films produced by vacuum arc is greater than that in the sputter deposited films. Such a high oxygen content can be attributed to a higher residual pressure in the chamber combined with the high reactivity of titanium as well as to the pulsed nature of the deposition process. The variation of the carbon peak shape and the intensity ratio of the two major titanium peaks in the

AES spectra are good indicators of the bonding state of the two elements as shown previously [10]. As expected, the proportion of C-C bonds increases with decreasing duration of the titanium plasma pulse and with increasing concentration of CH_4 in the gas phase. For the sputtered films, the proportion of C-C bonds for a given global composition is strongly influenced by the discharge current density. This is related to the decomposition of the C precursor in the plasma and to the larger mobility of atomic species in comparison with the mobility of molecular fragments on the surface of the growing film. For the vacuum arc deposited films, the influence of the ion energy on the bonding states is complex and varies with the global composition [11], but it does not affect the proportion of Ti and C in the films. At high carbon concentrations, increasing the ion energy promotes the C-C bonding but this effect is not observed for nearly stoichiometric films.

The hydrogen content of the sputtered films was not determined but studies showed that the incorporation of hydrogen is linked to the amount of amorphous carbon present in the films.

Depth profiling combined with AES analysis and RBS proved that the sputtered films are particularly homogeneous in depth and that the interface with the substrates are sharp (figure 1). For the vacuum arc deposited films, the same analysis showed that the titanium depth distribution is not uniform. The films are richer in titanium at the surface than at the silicon interface. This is due to a faster decrease in efficiency of the carbon plasma source than of the titanium source. This decrease can be reduced or compensated by changing the source

geometry or by varying the pulse duration ratio during the deposition. The width of the interface is strongly related to the bias voltage as shown in figure 2. This behavior is explained by the larger implantation depth of ions accelerated by a high bias voltage. The interface width can be simulated with the T-DYN [13,14] model that takes into account the average charge of the ions, 2.1 for Ti and 1.0 for C, and the nature of the substrate.

Microstructure

XRD, high resolution electron microscopy and selected area electron diffraction indicated a strong correlation between the crystallite size and the carbon concentration in both types of films. The grain size diminishes quickly with increasing carbon concentration. At high carbon concentration, the films consist of nanocrystals of TiC dispersed in an amorphous carbon matrix. In both cases, the excess carbon is accommodated first in interstitial sites in the B1 structure, modifying the lattice parameters of TiC as we observed in the diffraction patterns, and then forms an amorphous carbon phase if the carbon concentration is further increased. For similar Ti:C ratio, the grain size is slightly larger for sputtered films than for vacuum arc deposited films.

A major difference in the preferential orientation of crystallites is observed in films close to stoichiometric composition prepared by the two techniques: <111> for the sputtered films and <100> for the vacuum arc films. A more detailed study of the growth mechanisms is necessary to explain this

difference. It could be related to the difference in ion deposition energy in the two processes.

Mechanical properties

The film stress was measured exclusively for films prepared by vacuum arc technique. The effect of Ti incorporation on the stress is quite remarkable, as indicated in figure 3 for four compositions and three bias voltages. Small additions of titanium reduce drastically the stress in comparison with that observed in pure amorphous carbon films. The stress is even lower than that observed for stoichiometric TiC films. The lower stresses are observed for the highest bias. Those films did not show any relaxation during annealing up to 650 K. On the contrary, films prepared at a bias of -100 V showed strong relaxation upon annealing at much lower temperatures. The behavior of films prepared at a bias of -500V depended on the film composition. It is interesting to note that the observed stress directly correlates with the number of Ti-C bonds in the films and therefore with the proportion of the crystalline phase.

The results of pull tests are mostly comparative. Table 2 summarizes the observations. The maximum load that was applied is of order 50-70 MPa and corresponds to the strength of the epoxy glue. Films deposited at high bias voltages by the vacuum arc technique are always adherent. The diffuse nature of the interface in these cases is responsible for the good adhesion of these films. The only adherent sputtered films were those presenting a crystalline TiC phase.

As soon as the proportion of amorphous carbon phase increased, the films delaminated either spontaneously (very high carbon content) or under very small load.

Figure 4 presents a comparison of the variation of the friction coefficient with the number of rotations for three sputtered films of different compositions. The best results are observed for the film with the composition closest to stoichiometry. All films failed in a similar way: they first wear off and suddenly present a massive adhesive failure. These observations are consistent with the adhesion measurements. The most adherent film is that lasting the longest in the wear experiments. In all cases, the wear scars on the balls were barely measurable. The dominant feature is the debris transfer on the ball. A comparison of the wear behavior of films prepared by the two technique and of similar composition (close to stoichiometry) is given in figure 5. The two curves are shifted vertically relative to each other. They are very similar. The progressive increase of the friction coefficient is associated with the wear of the coating and the accumulation of debris in the wear track and on the ball. After a comparable number of rotations, we observe an adhesive failure of both coatings. From the point of view of the wear test, the diffuse interface of the vacuum arc deposited films, the incorporation of hydrogen in the sputtered films, and the difference in preferential orientation of the films prepared by the two techniques, surprisingly do not play a major role.

IV. Conclusions

TiC_x films were successfully prepared over a wide range of composition by both techniques. The morphology and crystallinity of the deposited films are modified by the carbon content and its bonding states. The excess carbon is accommodated in interstitial sites in the B1 structure or forms an a-C phase. This phase induced the reduction of the TiC grain size. The lack of adhesion encountered in the sputtered films containing a large excess of carbon was overcome in the vacuum arc films by providing high energy to the depositing ions. The use of high energy ions results in a broad interface that enhances the adhesion of the films.

The major composition difference was the incorporation of hydrogen in the sputtered films. The texture of the films prepared by the two techniques differed: <111> for the sputtered films and <100> for the vacuum arc films. The wear behavior of films with similar Ti:C ratios is comparable despite the difference in microstructure and structure of the interface.

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Table captions:

Table 1: Variation of film composition, and bonding states of C and Ti atoms as a function of the process parameters.

Table 2: Comparison of the adhesion for films prepared by the two techniques

Figure captions:

Figure 1: RBS titanium distribution profiles for two films prepared by reactive magnetron sputtering

Figure 2: Variation of the RBS titanium and oxygen distribution profiles with bias voltage for vacuum arc deposited films

Figure 3: Variation of the stress of vacuum arc deposited films as a function of the Ti:C pulse duration ratio and the bias voltage

Figure 4: Comparison of the variation of the friction coefficient during ball-on-disk tests for three films prepared by reactive magnetron sputtering

Figure 5: Comparison of the variation of the friction coefficient during ball-on-disk tests for two films of similar composition prepared by vacuum arc and reactive magnetron sputtering

Table 1 :

Film composition	CH_4 / Ar vol.%	pulse duration ratio C/Ti	Bonding of Ti	Bonding of C
Sputtered films				
$Ti_{0.4}C_{0.6}$	12.7		carbide	carbide + trace of a-C:H
$Ti_{0.2}C_{0.8}$	17.5		carbide	carbide + a-C:H
$Ti_{0.05}C_{0.95}$	24.0		carbide	a-C:H + trace of carbide
Vacuum arc films				
$Ti_{0.6}C_{0.4}$		1:1	carbide + metal	purely carbide
$Ti_{0.55}C_{0.45}$		1:2	carbide	carbide + trace of a-C
$Ti_{0.35}C_{0.65}$		1:4	carbide	carbide + a-C

Table 2:

film composition	adhesion
sputtered films	
$Ti_{0.4}C_{0.6}$	good
$Ti_{0.2}C_{0.8}$	good
$Ti_{0.05}C_{0.95}$	very poor
vacuum arc films	
$Ti_{0.6}C_{0.4}$	good
a-C	good