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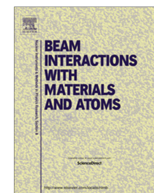

Surface layer evolution caused by the bombardment with ionized metal vapor

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ABSTRACT

The evolution of the composition of tungsten carbide and silicon surfaces initiated by the bombardment with Zr and Cr ions has been investigated as a function of the substrate bias voltage. Surface composition profiles were measured by Rutherford backscattering and have been compared with the results obtained by the TRIDYN simulation program. It is found that the general dependence of film thickness on substrate bias is satisfactorily reproduced by this model. Deviations between experiment and simulation are attributed to possible partial oxidation of the surface or uncertainties in the charge state distribution of metal ions. The results confirm that TRIDYN facilitates the predictability of the nucleation of metallic vapor at substrate surfaces.

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1. Introduction

Coatings synthesized by cathodic arc deposition have been utilized in industrial production since a few decades (see review in [1, Chapter 2]). The high degree of ionization of the metallic vapor generated by the cathodic arc allows a control of the condensation and layer forming process at the substrate surface. In combination with the substrate bias, the microstructure of the coatings and their mechanical properties can be influenced. Of particular interest in Physical Vapor Deposition (PVD) is the formation of substrate-coating interfaces. Because layer growth in PVD proceeds under non-thermal equilibrium conditions, large stress is frequently generated during the initial steps in layer formation. Interfaces are therefore critical regions with respect to adhesion and mechanical stability. Pre-treatment procedures of substrate surfaces under vacuum were developed with the intention to clean substrate surfaces and to stabilize the substrate surface. Ionized metallic vapor has been utilized with great success to improve coating adhesion, not only for coatings deposited by arc technology, but also in combination with e.g. sputter deposition [2–4]. In this process, the substrates are biased with typically −1000 V to −1200 V which results in an etching of substrate material and the incorporation of the metal ions in the near surface region of the substrate. To distinguish from the standard etching process based on Ar ions obtained from glow discharge, this process was named as metal ion etch (MIE).

The predictability of the MIE is complicated by macro-particles (or "droplets") which are always a by-product of cathodic arc evaporation and, additionally, by neutrals. To increase sputtering, argon is usually added to the arc discharge, which again influences the etching result. The utilization of the filtered arc for deposition and etching had been studied by Aksenov et al. [5] already before the above mentioned MIE approaches. In that work the condensation of Al ions was investigated and it was found that deposition and etching rates balance each other at about – 500 V substrate bias. It was also shown that the addition of oxygen changes the condensation rate of the Al ions.

The investigations in the present work are aimed to control the condensation of Zr and Cr ions at different substrate types. The ions were produced by the cathodic arc operated behind a fixed shutter. The shutter prevents the substrate surface from deposition of droplets and neutrals. This approach to generate the "filtered" ion beam is by far simpler compared with the filtered arc in [5]. The bombardment energy of the ions was varied by the bias potential applied to the substrates. The study should give an answer on how controllable and predictable the treatment of substrate

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surfaces by ions is. It has been shown in the past, that TRIDYN simulations are helpful to explain effects in plasma immersion ion implantation and pulsed cathodic arc deposition [6,7]. Therefore, the areal density of the ions measured by RBS has been compared with TRIDYN simulations.

2. Experimental

The experiments were performed in an INNOVA batch-type production system of OC Oerlikon Balzers AG which is schematically shown in Fig. 1. The arc operation was initiated once a total pressure below $2 \cdot 10^{-4}$ mbar was reached in the deposition system. Zr and Cr cast targets (manufactured by Gesellschaft für Elektrometallurgie mbH) were utilized as cathodes. The targets were operated with a DC power supply and currents of 200 A and 140 A, respectively. The arc discharge was self-sustaining, which means that no additional gases are added to the arc discharge. A fixed shutter was used to prevent a deposition of droplets at the substrate. During arc operation, the chamber pressure drops below 10^{-4} mbar due to gettering. Because no additional gases are added to the arc discharge and gas scattering is unlikely, one can expect that the contribution of neutrals to layer formation is negligible. However, this was not inspected and can therefore not be completely excluded. For the substrate treatment, the ions extracted from the arc discharge were utilized. Typical ion currents between 1 and 2 A were achieved with this set-up. The substrates were mounted on substrate holders and experienced a twofold rotation during ion bombardment. A DC substrate bias between −20 V and −1200 V was applied to the substrate holder to adjust the energy of the ions. The substrates, pieces of (100) silicon wafers and polished cemented carbide inserts (WIDIA SPGN 120308, 94 wt.% WC / 6 wt.% Co), were wet-chemically cleaned before deposition. The substrates were not heated and their temperature did not exceed 100 °C for all treatments. An ion bombardment time of the substrate surface of 30 min was chosen.

The exposed tungsten carbide and silicon substrates have been analyzed by Rutherford Backscattering Spectrometry (RBS) [8] at the ETH Laboratory for Ion Beam Physics. Measurements have been performed using a 2 MeV ^{4}He beam and a silicon PIN diode detector under 168°. The collected data have been evaluated using the RUMP program [9]. Fig. 2 shows an example of the fitted RBS spectrum obtained for a Zr layer deposited on tungsten carbide deposited at room temperature with a substrate bias of 600 V. The resolution of the RBS measurement is not sufficient to resolve the exact depth profile of the material composition and the degree

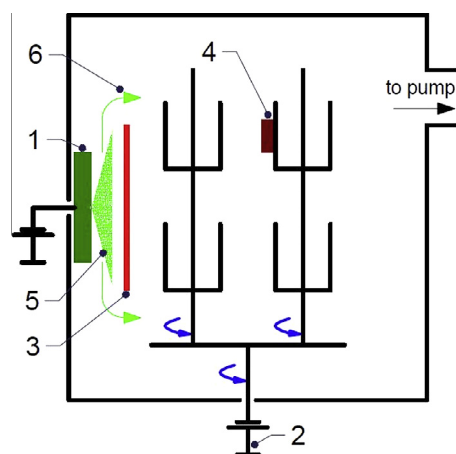

Fig. 1. Schematics of INNOVA cathodic arc deposition system. (1) Target for MIE, (2) bias supply, (3) shutter, (4) twofold rotating substrate for layer deposition, (5) evaporated target material, (6) ionized metal vapor without droplets.

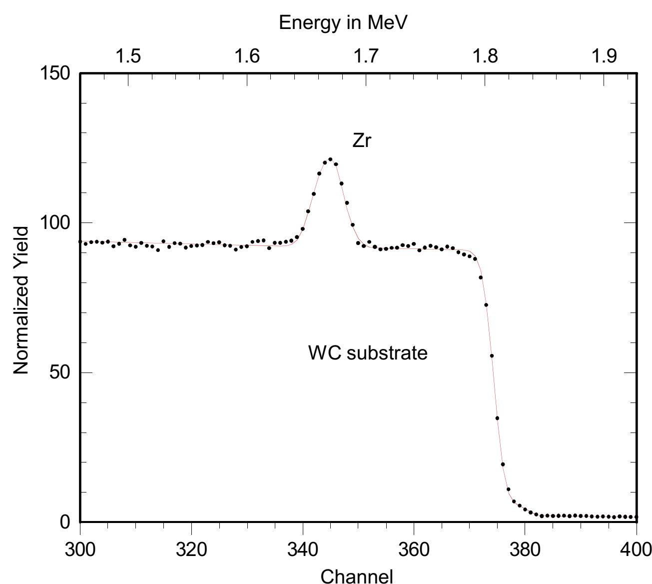

Fig. 2. RBS spectrum of a Zr layer deposited on tungsten carbide.

of implantation or subplantation of the layer. Therefore, only the net area density in number of atoms per cm^2 has been determined.

3. Simulation

The compositional evolution of the substrate surface as a function of fluence and bias voltage has been simulated using the TRIDYN Monte Carlo code [10] which is based on the TRIM/SRIM program [11]. TRIDYN simulates the stopping of incident particles in the substrate using the binary collision approximation. The dynamic change of the surface composition is calculated by taking into account ballistic effects such as projectile deposition and reflection, sputtering, and ion beam mixing [12].

Fig. 3 shows and example of atomic concentration profiles and total coverage calculated by TRIDYN for Zr atoms incident on a WC surface. Several important features can be observed. The concentration depth profile for a substrate bias of 1000 V and a Zr fluence of $8 \cdot 10^{16}$ cm^{-2} shows that initial preferential sputtering of carbon atoms leads to an enhancement of tungsten at the well intermixed interface. Above a fluence of approximately $1 \cdot 10^{17}$ cm^{-2} the fast growth of the implanted layer is reduced, a steady state of implantation and resputtering is reached with a Zr sputtering yield of 0.85 and the growth rate decreases to about 0.3 nm per 10^{16} incident Zr atoms per cm^2. Fig. 3c shows that the steady state growth rate is strongly dependent on substrate bias. Above a voltage of approximately 1500 V the sputter yield of Zr in the film surface becomes 1 and the layer reaches a constant Zr coverage under steady state conditions. Since also W and C are sputtered away the surface is constantly receding.

In the most recent version of TRIDYN an individual energy spectrum can be defined for each primary particle species. This allows a variation of the charge state distribution of the metal ions in MIE. TRIDYN is able to calculate the depth profiles of atomic concentrations at much higher resolution than obtained by the RBS technique. Therefore, only the total area density of metal atoms (Zr, Cr) in atoms per cm^2 of simulated profiles has been compared to the integrated surface coverage extracted from the RBS spectra.

4. Results and discussion

The onset of layer growth on Si and WC substrates during MIE has been investigated as a function of substrate bias for pure Zr

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