Adhesion Improvement of PVD Coatings by Plasma Treatment with Linear Anode Layer Ion Sources

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ABSTRACT

The pre-treatment of workpiece surfaces is decisive for improved adhesion of tribological, decorative, sensor, biocompatible, etc. coatings subsequently deposited by vacuum coating techniques. Most current industrial techniques (mainly glow discharges) don't meet the requirements for activating temperature-sensitive and electrically insulating materials. Gridless plasma and ion sources – like the linear anode layer ion source used in this work – are an excellent alternative due to their low investment and operating costs and scalability to many industrial applications. The appreciable increase of adhesion by anode layer source plasma pre-treatment and the effects of ion energy and dose are shown for magnetron sputtered titanium nitride coatings on AISI D2 tool steels at room temperature.

INTRODUCTION – TECHNIQUES FOR ADHESION IMPROVEMENT

The adhesion of thin films on surfaces is influenced by various properties including substrate roughness and cleanliness, film stress and structure, and thermal/mechanical properties of the substrate and film. Thus, the choice of substrate and film materials as well as substrate pre-treatment and coating technique are critical for achieving highly adherent coatings [1-3]. While the materials are usually determined by the application, pre-treatment and coating technique attach great importance in industrial coating practices.

The application of plasma and ion beams for pre-treatment has been successfully applied to improve adhesion of various PVD and CVD deposited coatings by pre-cleaning in a variety of studies on different substrates, such as glass, metal, and plastic [4,5]. The interaction of energetic ions with the solid surface leads to the following effects:

1. reduction of surface contamination and formation of a chemically homogenous surface which is free of surface contaminants and debris from previous manufacturing steps or storage
2. roughening of the surface increasing the interfacial surface area between substrate and film as well as formation of mechanical interlocking sites
3. chemical activation of the surface (e.g. oxidation) [6].

All these macroscopic effects are accompanied by microscopic interactions. Energy transfer from energetic ions to substrate atoms leads to several microscopic effects. Ion implantation changes the chemical composition of the sub-surface zone resulting in compound, alloy or mixture formation. Radiation damage of the surface lattice generates vacancies and interstitial atoms. If the energy transferred to surface atoms is higher than their binding energy, atoms are removed from the surface. The probability of sputtering is moreover dependent on the ion energy and mass as well as on the atomic composition of the solid surface, which results in preferred sputtering of one component of a compound surface and, thus, in non-uniform removal [7].

OVERVIEW OF CURRENTLY USED PLASMA ETCHING TECHNIQUES IN VACUUM COATING

A glow discharge is a simple method for producing a plasma at a substrate. In a glow discharge a gas is flowed into a region between two electrodes at different electrical potentials. The electric field in the region ionizes the gas particles creating a plasma. The workpiece (substrate) is typically attached to the negative electrode (cathode) which accelerates ions into the surface to remove contamination by sputtering. Plasma-generated radical species can also assist with the chemical etching of contaminants [8]. Glow discharges have limited process control in that ion energy and current density (dose) cannot be independently varied outside of a small range.

In contrast to glow discharges, ion sources produce a plasma and accelerate ions from it with electrostatic or electromagnetic forces. Ion sources provide independent control of energy and current over a much wider range. Two main types of broad-area ion sources are commonly used. Gridded ion sources produce a plasma in a discharge chamber and use electrostatic grids to accelerate ions toward the workpiece without requiring substrate bias [9]. A separate electron source neutralizes the ion beam to prevent substrate charging. The plasma generation in a gridded source is independent of the ion acceleration optics. Therefore any method can be used to generate the plasma, such as DC, RF, or microwave. Gridded ion sources provide a high degree of independent control of ion energy and current. The ion beam is mono-energetic, allowing the selection of specific ion energies for process optimisation.

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However, despite the maturity of gridded ion source technology, these instruments have a high degree of complexity and require substantial maintenance to operate as process tools due to the lifetime of grids and the electron source. As an alternative, gridless ion sources offer an elegant solution to ion beam production. Gridless ion sources have many fewer parts and reduced maintenance requirements. One type of gridless ion source is the so-called anode layer source (ALS) (Figure 1a). To produce a plasma, two cathode plates focus a magnetic field in the gap in front of the anode. The magnetic field restricts the motion of electrons emitted from the cathode as they drift toward the anode. The electrons instead move parallel to the anode along the channel between the cathode plates where they ionize a working gas that is injected into the anode region. The low mobility of the electrons in the direction of the anode forms an electric field that accelerates plasma ions out of the source. The kinetic energy of the individual ions is some fraction of the voltage applied to the anode and is determined by the position in the potential field at which the ions are created. Unlike the gridded source, the resulting ion beam has a broad ion energy distribution. Beam ions create secondary electrons to sustain the discharge by collisions with the cathodes and downstream surfaces. The accelerated ion flux draws electrons from the source plasma and is virtually self-neutralized. [10, 11].

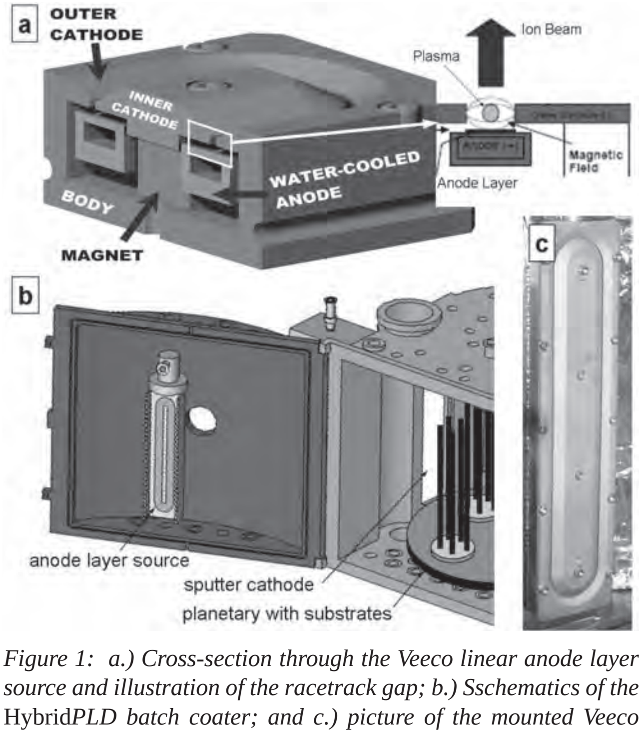

Figure 1: a.) Cross-section through the Veeco linear anode layer source and illustration of the racetrack gap; b.) Sschematics of the Hybrid*PLD batch coater; and c.) picture of the mounted Veeco ALS.*

The Veeco ALS used in this study can operate in vacuum pressures typically from 0.1 to 10 mTorr. The spectrum of ion energies ranges from nearly zero to the magnitude of the anode potential, which can generally be set in the range 0.7 – 3 kV. The mean ion energy is typically about 60% of the discharge potential (0.4 – 1.8 keV). The ion beam current density is typically 1-2 mA cm^{-2} directly over the plasma channel. Of more interest for linear sources used with in-line processes is the current produced per source length. The linear ALS can generate up to 15 mA cm^{-1} [12]. All together, The ALS offers a unique degree of flexibility and productivity in cleaning, surface modification, and deposition processes. The ALS is typically far more easily operated and maintained in a manufacturing environment than a grided ion source. Without the hindrance of accelerating grids and multiple electron source components, this device is considerably more robust, easier to maintain, uses fewer consumables, and may be powered with a single power supply. A unique feature of the Veeco linear ALS are sputter shields (patent pending) that drastically reduce iron contamination (< 0.1 %) of the treated surface compared to other commercially available ALS designs [13]. The sputter shields also produce extra electrons when struck by off-axis ions and enhance ion beam neutralization. Thus, the charging of electrical non-conductive substrate materials can be kept < 1 V.

EXPERIMENTAL

The applicability of the Veeco linear ALS for the pre-treatment of substrates for tribological coating was determined by choosing a combination of ALS ion treatment and DC magnetron sputtering of 2 μm thick titanium nitride (TiN) coatings. Thin titanium interface coatings were used to improve the adhesion of the TiN coatings deposited at room temperature. The sputtering was carried out at 1.8 kW from pure titanium targets in Ar-N$_2$ atmosphere. While the coating architecture was kept constant, the process parameters for the ALS ion treatment (acceleration voltage and time) were varied at constant pressure on moving substrates (polished and ultrasonically cleaned AISI D2 tool steel). To achieve deposition conditions close to industrial coating, the whole development was performed in the industrially-scaled *Hybrid*PLD deposition plant [14, 15] at Laser Center Leoben (Figure 1b).

The characterization of the samples was performed by light microscopy for determining the etching topography, by contact angle measurements with distilled water (20°C) for gathering information about the wettability, and by scratch testing (HRC diamond indenter with 200 µm tip radius, 20 mm/min scratch speed between 5 – 50 N) for determining the film adhesion. The analysis of the scratches for finding the critical load for delamination was based on acoustic emission, normal and friction forces as well as on microscopic investigations. In addition, the intrinsic stress of the films was determined by X-ray diffraction (XRD) on a Bruker AXS D8 diffractometer equipped with a CrKα X-ray source. For stress calculation from the peak shift (stretching of the TiN lattice) a Poisson's ratio and an elastic modulus of 0.2 and 250 GPa were assumed, respectively.

RESULTS AND DISCUSSION

Surveying the etching effect in dependence on the treatment duration (Figure 2) reveals a significant improvement compared to untreated samples (0 min). First of all, long plasma etching leads to increased roughness by exposing the primary carbides (as shown on the backscattered electron image taken by scanning electron microscopy (SEM), Figure 2b). This effect is caused by different sputter etching rates of the martensitic matrix and carbides in the steel as theoretically proved by SRIM calculations (stopping range of ions in matter [16]) for argon species with 1.5 keV kinetic energy. These calculations lead to ratios of Ni : Cr : Fe atom sputtering rates of 1.39 : 1.02 : 1.00. Thus, nickel atoms, found only in the matrix, are preferred sputtered, increasing the removal of the matrix. Additionally, stronger chemical binding – as evident for carbide phases – further decreases the sputtering of the carbides compared to the metal matrix. The extent of surface roughening is as strong that the structure of the etched surface is still visible after coating with 2 µm TiN (Figure 2c, near the scratch).

As a consequence, the roughening by preferred sputtering leads to a decrease of the water contact angle (Figure 2a) and, thus, to the favourable increase of wettability and decrease of surface energy. This effect is well known for hydrophilic surfaces (water contact angle < 50°) like steels, which are reflected by increasing wettability at higher roughness. (This is in contrast to hydrophobic materials. Additional low positive influence on the decreasing surface energy is caused by the surface chemistry, especially the changing composition of the covering oxide layer, immediately forming after removing the sample from vacuum.

Furthermore, the compressive intrinsic growth stress is decreased by the ion treatment (Figure 2a); the reasons therefore will be discussed later. A contrary influence is found for the critical load to delamination in the scratch test (Figure 2a). This increase in adhesion was characteristically found for several other steels of high hardness (> 40 HRC) [17]. The beneficial type of cracking in the coatings – semicircular cracks against the scratching direction – is typical for tough coating materials and, thus, surprising for the room-temperature sputtered TiN coatings. Such cracks are caused by (elasto-)plastic deformation under the applied load, resulting in piling-up and rising of material in front of the moving indenter leading to tensile stress on the surface [18]. Thus, the intrinsic compressive stresses of the coating are superposed by tensile stresses. If the tensile strength of the coating is exceeded, this leads finally to cracking through the coating. If there is no further crack growth along the interface between coating and substrate, the characteristic parallel lines in the scratch track are visible. For the analysis of the critical load, these cracks were not included, because their formation does not describe the interface but only the coating behaviour (toughness) itself. The critical load is reached, if cracks are spreading along the interface and, thus, the coating is flaking off. This large-area delamination was localized directly at the interface between the (etched) substrate and titanium interface layer in scanning electron microscopy analysis. However, longer cleaned and, thus, rougher surfaces lead in all cases to increased adhesion.

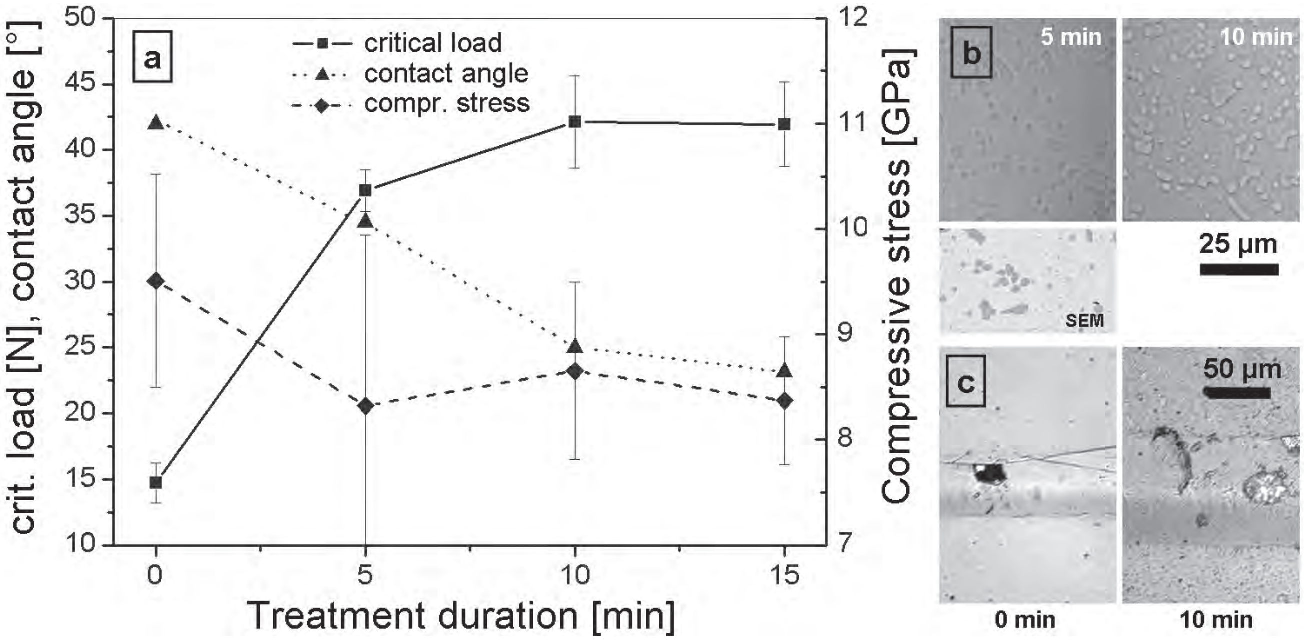

Figure 2: Influences of the Veeco ALS treatment duration at 3 kV anode potential on: a.) the water contact angle of a AISI D2 tool steel surface as well as on the intrinsic compressive growth stress and on the critical delamination load in scratch testing of a 2 µm thick subsequently to the ion treatment at room temperature sputtered TiN coating; b.) the roughness and structure formation on the surface; and c.) the first delamination occurring during scratch testing at the critical load.

Besides the treatment duration, the influence of the anode potential was investigated (Figure 3). The anode potential is directly proportional to the average ion energy of the ion beam (about 45 to 60 % of the anode potential or acceleration voltage). As expected, a significant roughening of the surface is observable at increasing anode potential (Figure 3b), while scarce information can be gathered from the contact angle measurements. Furthermore, ion treatments up to 2 kV anode potential (about 1.2 keV average ion energy) increase the critical delamination load (Figure 3a). Higher anode potentials (3 kV) result in decreasing adhesion and increasing compressive intrinsic growth stresses, although the film structures and textures are nearly identical. The characteristics of cracking in the coating in front of the moving indenter (Figure 3c) are similar to the phenomenon described above. To find the explanation for this behaviour the following effects of ion bombardment of energies between 100 and 2000 eV have to be taken into consideration: (1) formation of energetic peaks by particles between 100 and 1000 eV (displacement of particles at the surface and 1-3 nm underneath), (2) sputtering from the surface by ions > 100 eV (highest effect at some keV), and (3) the implantation into the bulk by ions > 1 keV (highest effect at some 10 keV). The sputter etching effect helps decisively to remove oxides from and to roughen the surface, finally decreasing the compressive stress at anode potentials < 2 kV. Higher anode potentials will result in higher probability to deeper implantation (> 5 nm based on SRIM calculations for 1.8 keV ion energy (~ 3 kV anode potential)). In combination with channelling of ions in open lattice directions (low density of atoms) the implantation depth can be further extended. Lattice distortion by the implanted atoms leads to a compressive stress increase at the substrate surface, complicating the relaxation of the film growth stress by deformation just beneath the surface compared to ion treatments at lower anode potential. Thus, the compressive stress in the films increases too as found in stress measurements. Higher film stress as well as lower deformability of the interface-near region result finally in the lowered critical delamination load. As shown above, the treatment duration (at the 3 kV) scarcely influences the adhesion assuming a rather equal thickness of the implanted layer for the investigated treatment durations.

CONCLUSIONS

The ion and plasma treatment (e.g. by glow discharges) is a state-of-the-art technique for improving the film adhesion in industrial vacuum coating, although major problems exist in the application for temperature sensitive and/or electrical non-conductive materials (e.g. polymers). To overcome these problems, gridless ion sources (like the anode layer source) were developed in recent years, presenting a real alternative for industrial applications due to their simplicity in construction and use as well as their easy scale-up.

This work revealed the successful application of a gridless Veeco linear anode layer source for pre-treatment (ion etching) of AISI D2 tool steel substrates before room-temperature magnetron sputtering of wear-resistant titanium nitride coatings. The results revealed a dramatic increase of coating

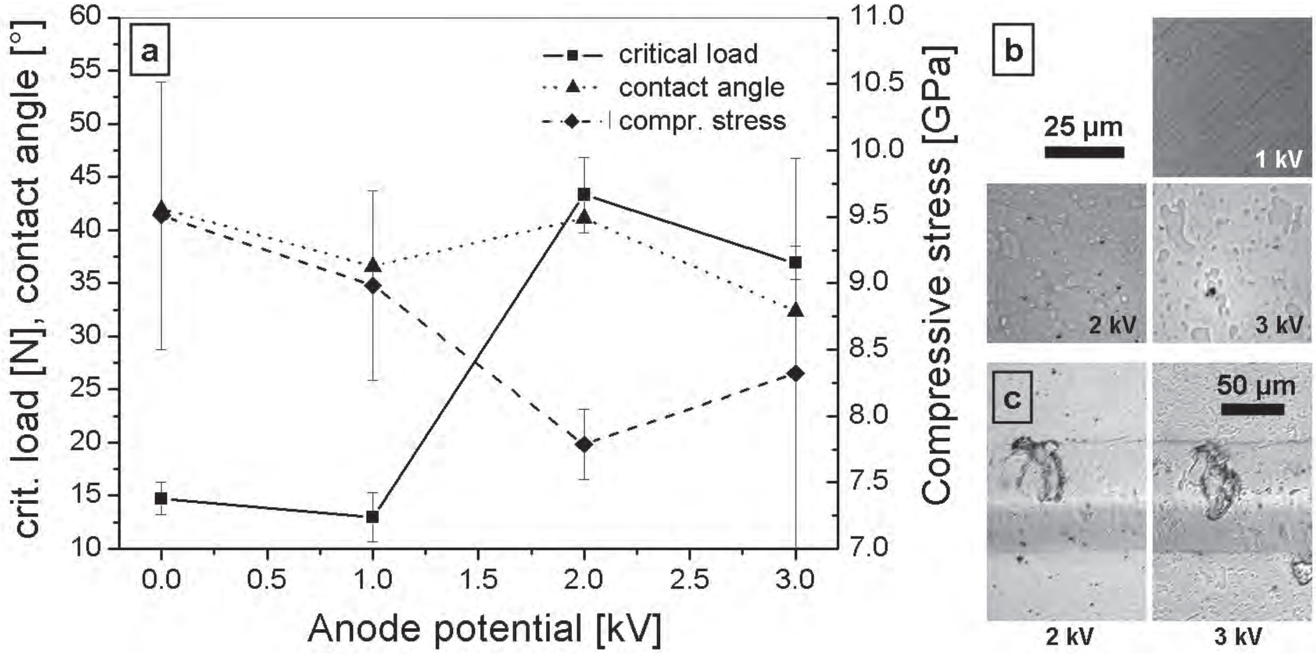

Figure 3: Influences of the Veeco ALS anode potential for 5 minutes treatment duration on: a.) the water contact angle of a AISI D2 tool steel surface as well as on the intrinsic compressive growth stress and on the critical delamination load in scratch testing of a 2 µm thick subsequently to the ion treatment at room temperature sputtered TiN coating; b.) the roughness and structure formation on the surface; and c.) the first delamination occurring during scratch testing at the critical load.

adhesion nearly independently on the treatment duration. Average ion energies of about 1000 eV allow best results due to sufficient sputtering of the surfaces for oxide layer removal and roughening as well as due to low tendency to ion implantation and embrittlement of the substrate surface. The discovered indirect correlation between film stress and adhesion strength goes hand in hand with the damage of the substrate surface and decrease in adhesion by high energetic ion treatment (average ion energy ~ 1.8 keV).

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