Metal Ion Beams for Sputter Cleaning and Deposition Assistance

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ABSTRACT

Ion beam sputtering of substrate surfaces prior to coating removes surface contaminants and oxide layers, substantially enhancing coating adhesion. In standard practice, sputtering is accomplished with a low energy beam of argon ions, as gas ion sources are readily available, argon is easy to ionize, and argon sputtering coefficients are fairly high. However, for high throughput applications, where beam currents on the order of several amperes are needed, the cost to vacuum pump the argon can become prohibitive.

High current, pure beams of metal ions can be produced by vacuum arc technology. As vacuum arc sources do not require any carrier gas, the problem of gas pumping is eliminated. In addition, it should be possible to partially implant the surface during the sputter cleaning to further enhance the adhesion by addition of coating-compatible metal. The same equipment can also be used in lieu of gas ion sources for ion beam assisted deposition. As the metal ions will be incorporated into the coating, the species can be chosen compatible with the coating - chromium for chromium nitride deposition - or to provide additional properties - yttrium to stabilize zirconium oxide. A dc, low voltage cathodic arc ion source has been developed, with ion beam currents in the ampere range even for very heavy metals, such as tantalum. The potential for this source for sputter cleaning and ion beam assisted deposition will be discussed.

INTRODUCTION

Use of the cathodic, or vacuum, arc for coating has been used commercially for many years. Brown, et al.,[1] demonstrated that the plasma produced by the cathodic arc is suitable for ion source applications, a technology that was commercialized by ISM Technologies in their MEVVA® series of metal ion sources. The MEVVA ion sources operate in the 80,000 volt range, with a pulsed arc. The beam currents extracted are up to 50 mA.[2][3] This combination of voltage and current is well-suited for metal ion implantation.

Further work with a dc arc source has resulted in the development of a cathodic arc ion source operating at low voltages (10 kV and below), with beam currents on the order of one ampere.[4] The energy and current of this ion source are sufficient for applications such as ion beam sputter cleaning, ion beam assisted deposition, and ion beam sputter deposition in production applications.

Serious consideration is being given to replacing electrochemical deposition means with vacuum coating processes for treating sheet steel for corrosion resistance. In most of these applications, the deposition is preceded by an ion cleaning step, and the deposition atoms are produced by evaporation. Other processing steps are used as well, including preheating with an electron beam.[5] It will be shown that a low energy, high current metal ion source can be used even in such high throughput systems.

SPUTTER CLEANING

An important part of all vacuum deposition processes is cleaning of the substrate. The most effective cleaning process is sputtering. For cathodic arc deposition, this is carried out by biasing the substrate to around 1000 volts at the initiation of arc operation. Ions extracted from the arc plasma bombard the surface, effectively cleaning the surface prior to deposition.[6] In other coating processes, it has been found effective to bombard the surface with argon ions of 1 to 2 keV, where again the energy of the ions is produced by biasing the substrate.[7]

For many applications, where the substrate is an insulator (glass, plastic) or continuous sheet is to be coated, biasing techniques are not applicable. Sputter cleaning must be accomplished by bombardment of the surface with an ion beam at the appropriate energy, and preferably at low angle of incidence (the sputter coefficient of argon on iron at 30° is nearly three times that at 90°). The most common element used is argon, extracted from a gas ion source.

High current gas ion sources are quite easy to manufacture. However, metal ions have benefits over gas ions. To begin with, metal ions from an arc ion source are produced without any gas, therefore vacuum pumping requirements are substantially reduced when a metal ion source is used in place of a gas ion source. As shown in figure 1, the sputter coefficient for metal ions is higher than for argon, reducing the required beam current. Other, heavier inert gas ions (krypton, xenon) could be

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used in place of argon to increase the sputtering coefficient, but the cost of these gases makes this an uneconomical approach.

There is also the problem of entrainment of the sputter gas in the material surface, and in the coating itself. Of course, metal ions are more likely to be entrained in the surface. As in general the object is to improve the surface with a metal or metal-containing coating, this residue of metal in the surface can be made an advantage by proper choice of metal, enhancing coating adhesion.

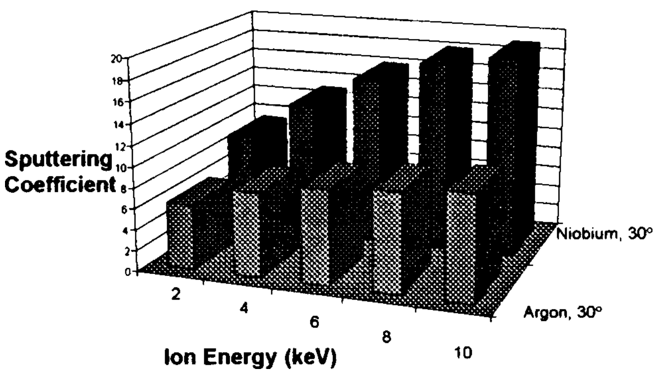

Figure 1. Sputtering Coefficient of Argon and Niobium on Iron at 30° Angle of Incidence

A single, one ampere ion source operating at 2 keV, with niobium ions, can clean surfaces at a fair rate. To estimate this rate, assume that the surface to be cleaned has an oxide scale approximately 10 nm thick, and that the substrate is a ferrous alloy. With the beam incident at 30°, the sputter coefficient on iron is 9.3. However, the oxide is harder to remove, so we assume a coefficient of 3. One ampere of ions is approximately $6x10^{18}$ ions/sec, so the rate of removal is three times this value, or $1.8x10^{19}$ atoms/sec.

If we assume a packing density of the scale of $5x10^{22}$ atoms/cm^3, a layer 10 nm thick and one square centimeter in area contains $5x10^{16}$ atoms. Dividing the removal rate by this value indicates that the source can clean 900 cm^2/sec.

ION BEAM ASSISTED DEPOSITION

During cathodic arc deposition, the substrate is biased to a voltage of approximately -100 volts. This bias voltage draws ions from the arc plasma into the substrate, enhancing the energy of the deposition and increasing coating adhesion and quality. The bombarding ions are mostly metal ions from the arc source.[8]

A substantial amount of work has been done on deposition via evaporation with ion bombardment supplied by an auxiliary ion source. Much as discussed above, gas ions, such as argon and nitrogen, can be used. If a reactive coating is to be formed, the gas pressure in the coating area will be high, and the additional gas from the source will not cause any additional pumping problems. Otherwise, the use of a metal ion beam could be important, particularly in preventing entrainment of gas ions in the coating. With a metal ion source, the impinging ions can be selected to be the same as the metal in the coating. They can also be selected to improve the performance of the coating. For instance, if the coating to be deposited is zirconium oxide, yttrium can be used in the ion source to form yttrium-stabilized zirconium oxide (YSZ).

For ion beam assisted deposition, the ions should impinge as close as possible to perpendicular to minimize sputtering. Higher energies are also of benefit - 10 keV versus 2 keV for cleaning. The higher energy is easier to achieve with metal ions, as the ions in the plasma from the cathodic arc are multiply charged. Niobium, for instance, has an average charge of +3. Thus, a niobium ion source would only require an ion source voltage of 3.3 kV to produce a beam of 10 keV ions.

We can estimate the area that a single ion source can treat if we assume that we need around one ion for every hundred atoms deposited on the surface, a rate that a number of researchers have found to be sufficient.[9] Assuming as well that the coating is to be 3 µm thick, and the coating density is $5x10^{22}$ cm^{-3}, the number of atoms in a square centimeter of surface is $1.5x10^{19}$. With these assumptions, we arrive at a rate of deposition of 40 cm^2/sec for a one ampere ion beam, well below the cleaning rate described above. Of course, the source of the deposition atoms must be able to keep pace with this rate.

ION BEAM SPUTTER DEPOSITION

As some high melting point materials are difficult to evaporate, the deposition material is often produced by sputtering. Where magnetrons and other such devices are not suitable, ion beam sputtering can be used. If a high current metal ion source is suitable for sputter cleaning a surface, it should also be suitable for ion beam sputter deposition. In this process, a beam of ions impinges on a target material at low angle. Material sputtered from the target deposits onto a substrate placed at a proper position with respect to the target. If the substrate is properly aligned, it is possible to bombard the substrate at the same time with the ion beam. Alternatively, a second ion beam can be used to assist the coating. As noted above, the ratio of assisting ions to deposition atoms is quite low, so the amount of beam needed to assist the deposition is far less than needed to produce the coating atoms.

Figure 2 is a bar graph of sputtering coefficients for 10 keV chromium and molybdenum ions at 30° incidence on aluminum, chromium, and zinc, three elements of interest for corrosion resistant coatings. As shown in table I, the rate of deposition for a 3 µm coating is quite low compared to the rate at which a single ion source can either clean a surface or assist

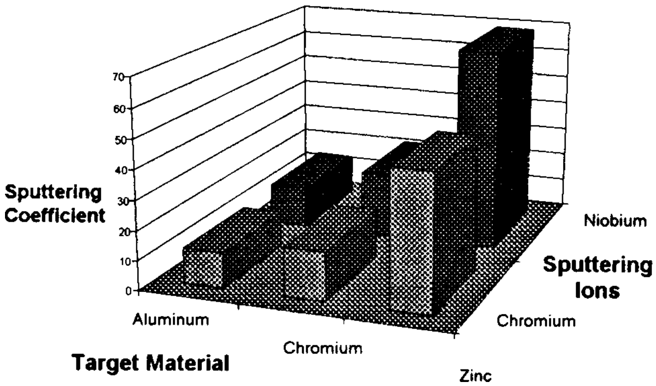

Figure 2. Sputtering coefficient at 30° incidence for 10 keV chromium and molybdenum ions on aluminum, chromium and zinc.

deposition. This low rate probably limits the use to deposition of materials which are very difficult to evaporate, i.e., elements with very high melting temperatures.

Table I
Rate of Deposition by Ion Beam Sputtering
Chromium Ions, 10 keV, 30° Incidence

Target Material	Aluminum	Chromium	Zinc
Beam Current (A)	1	1	1
Ions/sec	$6x10^{18}$	$6x10^{18}$	$6x10^{18}$
Sputtering Coefficient	12	16.5	46
Coating Density (g/cm^3)	2.7	7.1	7.2
Coating Density ($atoms/cm^3$)	$6x10^{22}$	$8.2x10^{22}$	$6.6x10^{22}$
Coating Thickness (μm)	3	3	3
$Atoms/cm^2$	$1.8x10^{19}$	$2.5x10^{19}$	$2x10^{19}$
Rate (cm^2/sec)	$1.2\ x10^{-3}$	$1.2\ x10^{-3}$	$4.1\ x10^{-3}$

If the coating were to be tungsten, for instance, with a tungsten ion beam of 10 keV, a one ampere ion source could ion beam sputter deposit a 3 μm coating at the rate of 0.002 cm^2/sec. This is a fairly reasonable rate for a material such as tungsten, which can only marginally be applied by other techniques.

DEPOSITION ON LARGE RIGID SURFACES

Figure 3 shows a general diagram of the use of ion beams for coating large areas, such as sheet steel or aluminum, or glass plate. Two ion beams are used. One beam, impinging at low angles sputter cleans the surface prior to deposition (the substrate moves from left to right), and, if the energy is high enough, deposits a small amount of metal at the surface to facilitate adhesion of the coating. A second ion beam impinges at near normal incidence on the surface during coating, increasing coating density, improving coating structure, and also enhancing adhesion. If the energy of these ions is high (greater than 5 keV), the ion bombardment will also keep the residual compressive stress in the coating low.

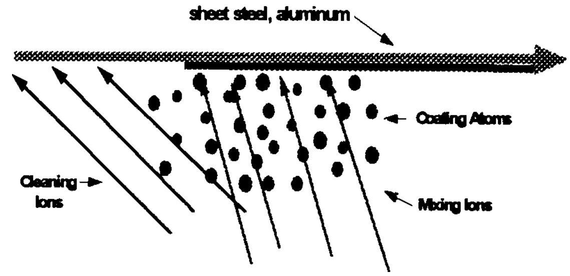

Figure 3. Conceptual diagram of continuous coating of sheet steel, aluminum, et al., combining metal ion beam sputter cleaning and metal ion beam assisted deposition. (Coating substrate moves from left to right.)

This combination of metal ion beam cleaning and metal ion beam assisted deposition offers a number of advantages over other processes, including superior coating quality, better energy efficiency, and lower gas pumping requirements. In addition, the simplicity of the process makes it easy to control and thus it is easy to maintain coating quality — perhaps the most important aspect of any process to be used for high-throughput systems.

LOW ENERGY DC ARC ION SOURCE (LEDA)

The cathodic arc is an excellent source of metal plasma for ion source applications. The plasma produced is pure, there is little un-ionized vapor emitted, and the degree of ionization is high, to the extent that the ions are multiply charged.

One of the drawbacks of the arc is that the current level is not continuous from 0 amperes on up. That is, the arc must have a minimum current for stable operation. This minimum is quite high, over 50 A. Approximately ten percent of that arc current is formed by ions. Ergo, for low current, high voltage ion sources, such as the MEVVA, the arc is pulsed. For low voltage ion sources, the cost to pulse the arc makes such sources far more costly than their gas counterparts, so the arc source is not a suitable for low energy, low voltage applications.

A second drawback of arc technology is that the arc produces particulates of the arc metal along with the plasma. These are called macro-particles, and range in size from a few to tens of μm in diameter. Coatings applied by cathodic arc are generally loaded with these particles. As they are not well bound to the surface, they represent problems for use of the arc for corrosion resistant coatings.

For use in ion sources, the macroparticles should not prove to be a problem. The time that the substrate is exposed to the surface for either sputter cleaning or ion beam assisted deposition is very small - seconds - compared to exposure during cathodic arc coating - hours - so the number of macroparticles incident on the surface is small.

Should the macroparticles prove to be a problem, they can be filtered out via magnetic fields. A number of different magnetic configurations have been developed to filter the macroparticles from the arc. [10] Such filtering has not been found to be viable for most commercial applications because it results in a significant lowering of arc efficiency. For an ion source, where the extracted current is far less than the ion current available from even the lowest current arcs, loss of arc efficiency is not a major problem.

With these considerations and applications in mind, ISM has developed LEDA, a low energy dc arc ion source. LEDA operates at voltages up to 5 kV, producing beams of metal ions with energies around 10 keV for most metals, and up to 15 keV for such heavy ions as niobium and tungsten. Beam currents as high as two amperes are possible, with beam current densities on the substrate of up to 5 mA/cm^2.

While the current ion source has a circular beam profile, an extraction system is in development that will produce a beam with a linear profile, most suited for continuous coating systems. Testing of this extractor should begin in a few weeks. Preliminary experiments have been conducted, and patents filed, on a macroparticle filter for LEDA as well.

CONCLUSIONS

Low energy metal ions are ideal for sputter cleaning surfaces or assisting coating deposition, and may even have value for ion beam sputter deposition. To this end, a low energy, dc cathodic arc ion source, LEDA, has been developed that could form the basis of a system to vacuum deposit coatings on sheet steel and other materials, eliminating chemically based, environmentally deleterious processes.

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