



## ION BEAM ENHANCED DEPOSITION OF HARD CHROME COATINGS

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### *Abstract*

An advanced ion beam enhanced deposition process has been developed which is capable of depositing hard chrome coatings on most metallic, ceramic, plastic, and glass substrate materials. The hard chrome coatings are alloyed directly into the substrate surface thereby eliminating the need for the predeposition of interlayers and optimizing coating adhesion. The coatings are hydrogen-free and fully dense with a measured hardness exceeding 1100 Knoop (5 grams). Coatings up to 10 microns (0.0004 inches) thick can be deposited on components that are manipulated during processing to allow selective area coating and provide for a uniform coating thickness.

### *Background*

The deposition of metallic coatings such as chromium, nickel, and cadmium is usually achieved by wet chemical plating processes, and is done on a wide variety of engineered components and tools. There are however other techniques capable of depositing adherent metallic coatings that show much potential for use in the industrial marketplace if certain technological and economic hurdles can be overcome. Vacuum coating techniques, which were initially developed for the deposition of thin films in the electronic and optical industries, represent one class of deposition processes that are potentially attractive for the coating of mechanical components. The driving forces for investigating alternative deposition technologies include the need for improved coated component performance and the increasing pressures on reducing the environmental effects of chemical plating processes. Both of these issues can be addressed by vacuum coating techniques and form the basis for increasing interest in developing these processes.

There are five general classes of vacuum coating processes that can potentially be used for the deposition of chromium and other metallic coatings. All involve the production of energetic metal atoms or ions and the transport of those energetic metallic particles to the surface to be coated, either by electric fields or by using a plasma of energetic inert particles. The properties of the metallic coatings produced will be determined by the nature of the deposition process chosen. Thus not all of the processes can be used to deposit chromium (or other metallic) coatings that will have the desired engineering properties. The five general classes of vacuum deposition processes include vacuum evaporation (VE); sputtering (SP); ion plating (IP); direct ion deposition (DD); and ion beam enhanced deposition (IBED).<sup>1,2</sup> The key factors that differentiate the individual processes are the energy of arrival of the metallic atoms at the surface to be coated, and the degree of control provided by each process over this critical energy. This arrival energy will determine to a great extent coating morphology, residual stresses, physical properties, and adhesion.<sup>3-5</sup>

Figure 1 lists the relative energy ranges of the metallic atoms that reach the surface of a component treated with all five of the general classes of vacuum deposition processes. Vacuum evaporation is the lowest in energy of all of the vacuum deposition processes. The metallic atoms that reach the surface to be coated by vacuum evaporation have energies in the 0.1 to 1.0 electron volt (eV) range. At these energies the atoms come to rest on, and can move around the surface being coated. They begin to agglomerate at nucleation sites and a film coating grows. Coating adhesion is determined solely by van der Waals attraction and is usually not strong. Industrial applications of vacuum evaporation include web coating of thin mylar films with aluminum; fabrication of thin film electronic components such as resistors, capacitors, and strain gages; and coating of

optical elements such as lenses and mirrors with aluminum, gold, and silver.<sup>6</sup>

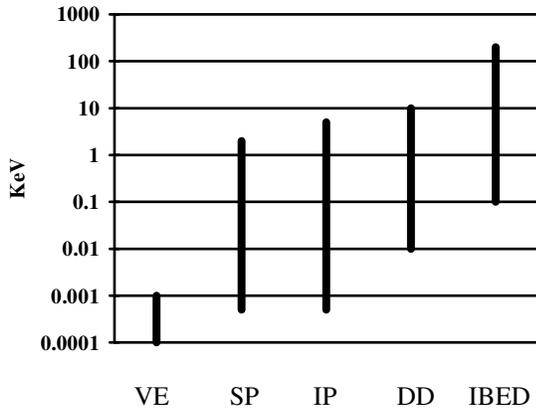


Figure 1. The arrival energy ranges of coating particles found with the five general classes of coating deposition processes.

Sputtering (DC, RF, or magnetron) is a higher energy process that utilizes a glow discharge to produce and transport coating atoms to the surface to be coated. Atomic particle arrival energies up to the 5 keV range are achievable, although the mean energies of the arriving atoms are two orders of magnitude lower. Atoms that arrive at the surface to be coated at these energies can react with the surface itself to form actual chemical bonds thereby improving adhesion. Pure metallic coatings as well as refractory nitride, oxide, and carbide coatings can be deposited with glow discharge based sputter coating processes. Sputter deposition is used primarily in the electrical component (integrated circuit) industry for the deposition of insulating and conductive thin films, and in the optical industry for the deposition of optical thin film coatings.<sup>7,8</sup> It is also used routinely for the deposition of decorative chromium coatings on plastic components for automobile and consumer products.<sup>9</sup>

Ion plating is a vacuum evaporation process assisted by a glow discharge. The ion plating process can be implemented in one of two major forms. Simple ion plating involves evaporation of coating materials (usually a metal like aluminum or gold) into a DC- or RF- supported glow discharge. The atoms of the metal coating material are transported to the surface to be coated, and a coating is grown. In reactive ion plating, a reactive gas is added to the glow discharge.

This produces a chemical reaction between the evaporated metal and the reactive gas. Compounds such as metallic nitrides can be formed by the chemical reactions and will condense on the surface to be coated. Simple ion plating is used primarily for the deposition of metallic coatings such as gold, silver, and aluminum. In one widely used ion plating process, aluminum coatings are deposited as an alternative to cadmium plating for corrosion resistance.<sup>10-12</sup> Reactive ion plating, also termed physical vapor deposition (PVD), is widely used to deposit hard coatings of titanium and chromium, nitride and carbonitride compounds. These coatings are routinely deposited on a wide variety of metallic tools and engineered components for increased wear-resistance.<sup>13</sup>

Since ion plating is a sputter-assisted deposition process, the distribution of coating particle energies is approximately the same as is found with glow discharge sputtering. Coating adhesion is determined primarily by chemical reaction at the surface being coated and is improved at elevated temperatures by thermal diffusion. One of the attractive features of ion plating is the increased rate of coating deposition. In general, most metals can be evaporated much faster than they can be sputtered. Thus much more material is liberated and available for coating growth and thicker coatings can be deposited at faster rates than can be deposited with simple sputtering.

Direct deposition of chromium and other metals has also been attempted in order to increase the energy of arrival of the coating species at the surface to be coated. The metallic species is first vaporized and ionized in an ion source, and then extracted at high energy by a high electrical potential.<sup>14-16</sup> Metallic particles with energies up to approximately 10 keV have been used to build coatings on the surface of various materials. Improvements in adhesion have been noted because of actual penetration of the accelerated atoms into the surface to be coated. The flux of atomic particles that can be produced economically with this type of deposition technology is low however, which limits the rate at which coatings can be produced. Thus even though direct deposition technology produces adherent coatings, and allows accurate control over the energy of the arriving particles, it is not a viable deposition technology for industrial scale-up.

Ion beam enhanced deposition is a relatively new deposition process that combines many of the

attractive features of the other classes of vacuum deposition techniques with the ability to deposit metallic coatings relatively rapidly, and with a high degree of control over the properties of the deposited coating.<sup>17</sup> The IBED process is a simultaneous thin film deposition with illumination of the growing film by a second, independently controllable, beam of energetic particles. A high vacuum environment is required for propagation of the secondary ion beam, which limits the thin film deposition technique used in the IBED process to either vacuum evaporation or ion beam sputtering. Since the secondary ion beam is independently controllable, the energy of the particles in the beam can be varied over a wide range and chosen within a very narrow window. This allows the energetics of deposition to be varied during the coating cycle and allows optimization of coating properties such as interfacial adhesion, density, morphology, and internal stresses. The wide energy range and controllable flexibility of the IBED process enable the deposition of chromium coatings on the substrate materials reported in this work.

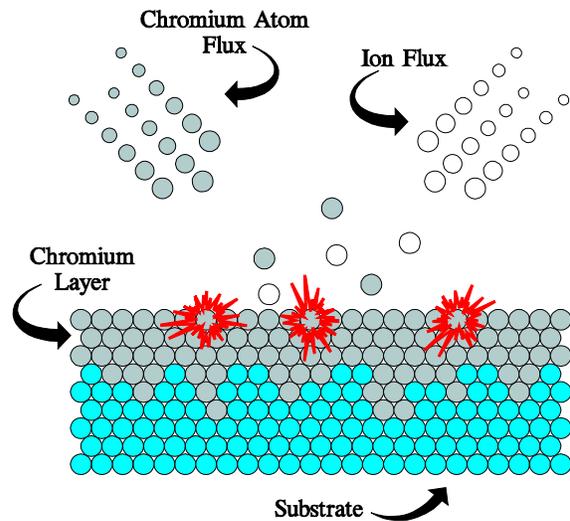


Figure 2. Schematic diagram of the implementation of the IBED process. Growth of a pure chromium coating is shown. Other metallic coatings, such as titanium, aluminum, copper, silver, and gold can also be deposited with the IBED process.

### *IBED Process*

Ion beam enhanced deposition (IBED) is carried out in a high vacuum, at pressures of  $1 \times 10^{-6}$  Torr or below. With proper choice of deposition parameters the temperature rise in components being processed can be held below 50 degrees Centigrade (92 degrees Fahrenheit). A general diagram of the implementation of the IBED process is seen in Figure 2. The surface to be coated is first illuminated with a flux of high energy inert gas ions that is initially used to remove surface oxides and other contaminants. This high energy flux is maintained, and once the surface is cleaned, a flux of pure chromium atoms is then directed simultaneously at the surface to be coated. The high energy inert gas ions are used to mix the initial few atomic layers of chromium into the surface being coated. This forms an alloyed bond layer in the surface that promotes adhesion of the chromium layer and is the mechanism that allows chromium coatings to be applied to virtually any substrate material without the need of an intermediate bonding layer of copper or nickel. Once the bond layer is formed properly, a chromium coating is then allowed to grow out from this bond layer. The high energy

inert gas ion flux is then used to control the morphology of the chromium coating that is being grown from the surface. This allows control over the grain structure of the coating as well as coating density and residual stresses. Chromium coatings in the thickness range of 5-10 microns (0.0002 - 0.0004 inches) can be grown with the techniques on most metallic, glass, ceramic, and plastic surfaces.

### *IBED Chromium Coatings - Characterization*

Chromium coatings have been deposited directly on a wide range of metal alloy materials. Figure 3 is a scanning electron micrograph (SEM) of a typical pure chromium coating deposited on a metallic surface, in this case, copper. Coupons cut from copper (C11000, electrolytic tough pitch) sheet were buffed and polished to a mirror finish and then cleaned in acetone and methanol solvents to remove residual buffing compound. The copper was then coated with a 5 micron (0.0002 inch) thick layer of chromium using the IBED process described above. The original polish on the copper coupon was maintained, and as can be seen in the SEM image, the chromium coating is smooth, continuous, and pinhole-free. Due to the nature of the IBED process the chromium

atoms that nucleate on the surface have a high degree of initial adatom

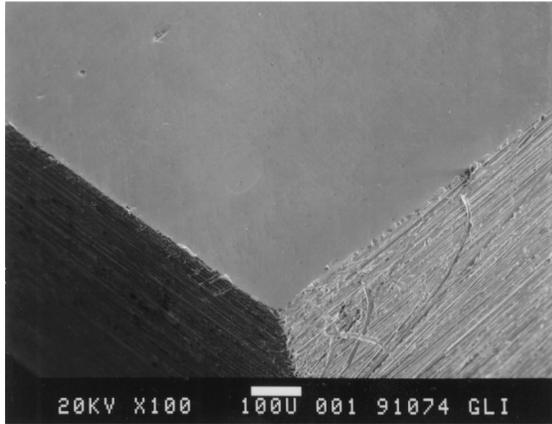


Figure 3. SEM image of a 5 micron (0.0002 inch) thick coating of pure chromium on a polished copper substrate. (SEM: AMR, Model 1000).

mobility and the coatings that subsequently grow replicate the finish of the surface being coated. Thus chromium coatings deposited on polished surfaces with the IBED process do not require post-coating polishing operations to restore the original surface finish.

The interfacial region between the IBED chromium coating and the copper substrate was examined by SEM and is pictured in Figure 4. An IBED chromium coated copper coupon was sectioned, mounted and polished using standard preparation techniques, and then imaged. The sample was not acid etched prior to imaging. The chromium coating is the uniform structure on top of the copper base material. The softer copper base material shows remnants of embedded polishing media and residual polishing marks and streaks. The chromium-copper interface appears very uniform with no evidence of delamination. The chromium coating itself shows no evidence of voids or cracks, and is smooth and featureless at this magnification (5000X). The brighter color of the uppermost region of the chromium coating is due to a focusing artifact from the SEM. The chromium layer is much harder than the copper substrate, which after grinding and polishing leads to a slight sample height variation between the uppermost layers of the chromium coating and the top surface of the copper coupon. Therefore when the chromium-copper interface is in

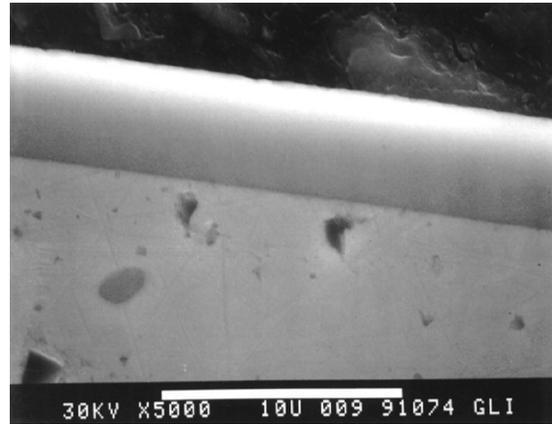


Figure 4. SEM image of the interfacial region at an IBED chromium coated copper surface. (SEM: AMR, Model 1000).

focus, the uppermost region of the chromium coating is out of focus and appears less resolved and brighter on the SEM image.

Further characterization of the IBED chromium coating was done by X-ray photoelectron spectroscopy (XPS) in order to assess the chemical purity of the IBED chromium. The XPS spectra of both the chromium layer and the copper substrate are displayed in Figures 5 and 6, respectively. The spectrum from the chromium layer clearly shows strong K-alpha (5.29 keV) and K-beta (5.92 keV) X-ray peaks characteristic of pure chromium metal. Spectral lines from other elements including aluminum, silicon, copper, oxygen, and carbon present in trace amounts were also detected. The aluminum and silicon are residual contaminants left from the sample polishing media (alumina and silica). Likewise, the presence of copper is due to smearing of the copper substrate into the exposed face of the chromium coating during sample sectioning and polishing. Trace amounts of carbon and oxygen are also present and are most likely remnants of sample polishing and mounting rather than contaminants introduced into the IBED chromium coating during deposition.

The spectrum from the copper substrate clearly shows the strong K-alpha (8.05 keV) and K-beta (8.86 keV) lines characteristic of pure copper. Also detected were peaks from aluminum, silicon, iron, and

chromium, all in trace amounts, and all probably remnants of the sample preparation procedure.

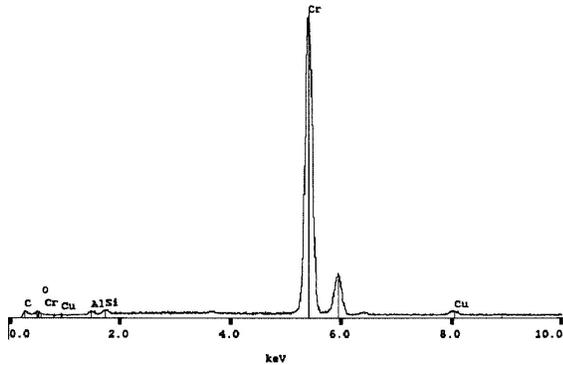


Figure 5. X-ray photoelectron spectrum from the IBED chromium layer. (Princeton GammaTech - IMIX Spectrometer).

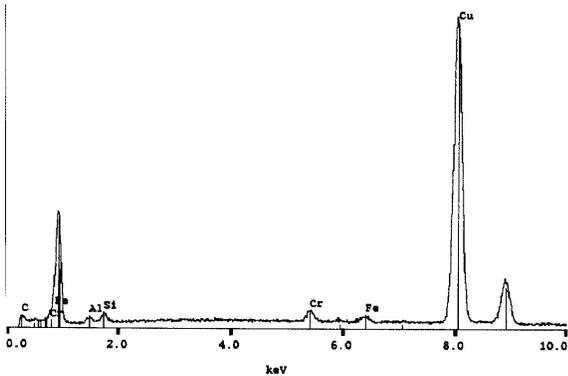


Figure 6. X-ray photoelectron spectrum from the copper substrate. (Princeton GammaTech - IMIX Spectrometer).

*IBED Chromium Coatings - Hardness*

The mechanical properties of IBED chromium coatings must be optimum in order for the process to be considered viable for use on engineered components. Since chromium is often specified for use as a hard, wear-resistant coating, the mechanical hardness of IBED chromium coatings was investigated. The IBED process was used to deposit pure chromium coatings on a variety of engineered metal alloy materials. The microhardness of the deposited coatings was then measured.

A set of samples was prepared from aluminum (6061), copper (110), carbon steel (1018), and alloy steel (4140) stock. Cylindrical coupons, 31.75 mm (1.25 inches) in diameter, and 19 mm (0.75 inches) long, were cut from rod stock. One flat face on each coupon was machined smooth and then lapped progressively with silicon carbide polishing media to a 15 micron (600 microinch) finish. Selected coupons were then lapped further with diamond paste to a 1 micron (40 microinch) finish. All sample coupons were then cleaned in acetone and methanol prior to IBED coating. Microhardness measurements of the surfaces of selected uncoated samples were made using a Knoop microhardness instrument (Torsion Balance Company: Kentron Microtester) at an indenting force of 5 grams.

Four prepared samples of each alloy material were then IBED coated with chromium. All sixteen sample coupons were coated at the same time with chromium to a thickness of 5 microns (0.0002 inch). The IBED chromium layer was deposited directly on the prepared surface of all sixteen samples without the use of any intermediate adhesion layers of copper or nickel. The temperature rise in the coupons during IBED coating did not exceed 50 degrees Centigrade (92 degrees Fahrenheit). The surface finish on all of the coupons IBED coated was not degraded. The 1 micron (40 microinch) finish on the polished samples remained shiny and optically reflective. The IBED chromium coating adhered tightly to the surfaces of all four alloy materials coated. Microhardness measurements were made on all coated samples and are listed in Table 1.

Table 1 Knoop Hardness Measurements

Material Type	Material Base Hardness (K)	Chromium Hardness (K)
Al - 6061	91.3	1121.7
Cu - 110	101.7	1085.1
Fe - 1018	326.1	1046.5
Fe - 4140	380.6	1008.5

The Knoop hardness measurements of the base material surface and of the IBED chromium coating are all averages of three separate measurements on each sample coupon. The Knoop hardness measurements are presented graphically in Figure 7.

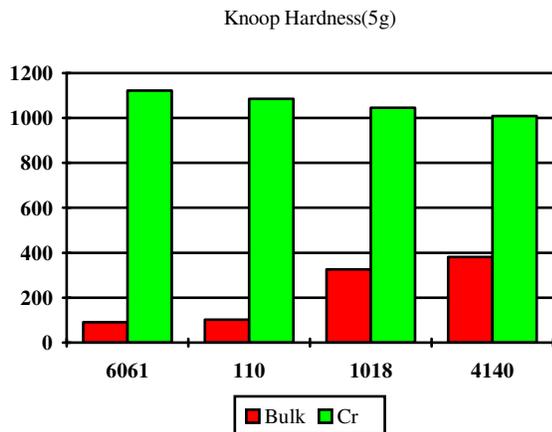


Figure 7. Knoop hardness measurements of the bulk material and the IBED chromium coating on each base material. The loading force used for these measurements was 5 grams.

### Results

Hard chromium coatings were deposited successfully on all of the aluminum, copper, and steel alloy materials investigated and tested in this experiment. No spalling or delamination of the coatings was found on any of the coated samples. Scanning electron microscopy showed the chromium coatings to be smooth, uniform, void-free, pinhole-free, and well bonded to the substrate. X-ray photoelectron spectroscopy showed the chromium coatings to be very pure and contamination-free. Knoop-scale hardness measurements of the IBED chromium coatings yielded an average that approached 1100 Knoop (5 gram). A number of individual hardness values exceeded 1200 Knoop (5 gram). In addition, the IBED chromium coating hardness was found to be essentially independent of the hardness of the base material on which the coating is deposited.

### Conclusions

A new, versatile ion beam based deposition technique has been developed which is capable of depositing hard chromium coatings on a wide variety of materials. The IBED technique differs from all other conventional vacuum deposition techniques in two

key ways. First, the energy of arrival of the chromium atoms at the surface to be coated is much higher with the IBED technique than is achievable with conventional vacuum deposition techniques. Second, since the IBED technique uses two independently controllable ion fluxes, the deposition conditions can be changed at different stages of the coating cycle. This provides the ability to produce adherent chromium coatings directly on the surface of a wide variety of materials, as well as the ability to control the morphology of the chromium coating produced. Chromium coatings with Knoop hardnesses exceeding 1100 (5g) were deposited successfully on aluminum, copper, and steel alloys. The new IBED technique shows much promise for use as a potential alternative to electrodeposition for depositing hard chromium coatings on engineered components of all types for improved part performance.

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