We have studied the modification of chromium coatings by nickel ion beams at a high energy (75 MeV) so that the range of the ions is many times the film thickness, which is of the order of 1 μm. At this energy, the rate of energy loss of ions is predicted to be fairly uniform over the entire thickness of the coating. The coating hardness increases significantly, even at moderate doses. The effect is stronger when the film deposition temperature is lower.

1. Introduction

For some years now, ion beam techniques have been applied in conjunction with vacuum coating technology to produce surface treatments that may have properties superior to those obtainable by the application of either technique alone. In one class of experiments, the two techniques are applied simultaneously and the ion beam assists the deposition. In this case, relatively thick coatings may be treated uniformly throughout their thickness. In another class of experiments, in which an ion beam is used to effect modification after the deposition of a coating, there is often a limitation arising from the fact that the range of ions is small compared to coating thickness in cases of practical interest.

In our studies we have chosen a variation in the approach to modifying a coating by ion irradiation. A high energy, at which the range is many times the coating thickness, is employed. Thus, end of the range effects are placed deep inside the substrate rather than at the interface. The details of energy loss mechanisms at high energies then become relevant to the prospects of coating modification. It is possible to set up conditions so that any effect will take place uniformly throughout the depth of a relatively thick coating. We have previously reported improvements in the adhesion of chromium films using this approach and in this paper present a study of changes in film hardness.

2. Experimental procedure

Chromium coatings in the range 1–1.4 μm were deposited on polished SS304 substrates using an electron gun in a vacuum system employing a diffusion pump and liquid nitrogen trap. The chamber is heated prior to deposition, to degas the inner surfaces, and water-cooled during deposition. The pressure in the chamber drops to 5 × 10⁻⁶ torr. A shutter prevents exposure of the substrates during the initial phase of evaporation. Preparation of the substrates consisted of electropolishing followed by grinding and then diamond polishing. The final cleaning consisted of vapour degreasing in isopropyl alcohol. The vacuum system is provided with a radiant heater behind the substrates to provide heating when desired. The temperature can be measured using a thermocouple. Even when the heater is not used, there is a temperature rise due to some heat from the hearth. The temperature may vary from one substrate to another but is restricted to about 80°C when the substrates are unheated by the radiant heater. The deposition rate in the present work was 2–3 nm/s.

Nickel irradiation at 75 MeV was carried out on a 15UD Pelletron by selecting a charge state of 5. Figure 1 shows profiles of electronic energy loss, nuclear energy loss and range of ions for a 1.4 μm thick coating on SS304 calculated using the code TRIM. The electronic energy loss in the coating is fairly uniform in depth at 1.8 keV/Å and is over two orders of magnitude higher than the nuclear energy loss. This energy loss rate is the maximum
achievable for the present ion-target combination. Microhardness measurements were made using a Wolpert microhardness tester.

3. Results

Figure 2 shows the variation of microhardness with measurement load for coatings made on unheated substrates, before and after irradiation to a dose of $10^{13}$ ions/cm$^2$. The two curves for irradiated samples represent slightly different dose rates but the difference in hardness values is not appreciable. In either case there is a significant increase in hardness values, particularly at the lower loads. Figure 3 shows results for coatings deposited at 180°C for the same dose. Again, there is an increase in microhardness values following irradiation at various dose rates. In this case three widely different dose rates were used and there is now a noticeable dependence on this factor.

It is possible to convert the load dependence of microhardness values to display the variation of measured microhardness with depth of penetration of the indenter. Figure 4 shows converted data for the curve labelled 4.5 nA/mm$^2$ in Figure 2. Values obtained prior to irradiation and also prior to coating are included for comparison. In the curve for the irradiated case, one can see a relative increase in microhardness at depths less than the coating thickness. Although uncoated substrates hardened following irradiation under the same conditions, the hardening was relatively small and it is possible to deduce that significant hardening takes place within the film.

Figure 5 shows hardness profiles before and after irradiation at a dose rate of 1.2 nA/mm$^2$, for chromium film deposited without substrate heating for two widely different doses. There is an appreciable increase in hardness, even at the lower dose of $4.5 \times 10^{13}$ ions/cm$^2$.

4. Discussion

In Figures 2 and 3, one may compare the curves corresponding to a dose rate of 4.5 nA/mm$^2$. Following irradiation, the percentage increase in the microhardness measured at 10 g is over 90% for the film deposited without substrate heating and 70% for the film deposited at 180°C. Thus, the film deposited with intentional heating of the substrate exhibits a smaller change.

Thurner and Abergam$^1$ have shown that chromium films grown at room temperature or at 200°C contain significant intrinsic stresses of a tensile nature. However, the stress is considerably lower for the higher substrate temperature. Thus, there may be a common factor between the existence of these stresses and the mechanism, whereby the film undergoes modification on irradiation.

Hoffman$^4$ has discussed a grain boundary model for the origin of stresses. Atoms at a grain boundary randomly take on a range
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Figure 5. Microhardness vs load for 304 stainless steel coated with Cr without substrate heating, measured before and after Ni irradiation at 75 MeV to doses of $4.5 \times 10^{13}$ ions/cm$^2$ and $2 \times 10^{13}$ ions/cm$^2$, at a dose rate of 1.2 nA/mm$^2$.

An important factor in deciding the likelihood of a thermal spike is the localisation of electrons that are ejected by the incoming ions. In a periodic lattice, elastic scattering is limited and electrons travel large distances, losing energy only by further excitation of electrons. However, on the model mentioned above, the grain boundary region contains a non-periodic potential. This may cause localisation of the energy transferred in an electronic collision due to increased elastic collisions of the ejected electron. This could be a possible model for structural modifications. Any modification at the grain boundary would alter the strain in the film, leading to possible changes in hardness.

5. Conclusions

It is possible to increase the hardness of chromium films by high energy ion irradiation. Films deposited at a low substrate temperature, which are expected to have higher stress levels, undergo a greater degree of change. There are appreciable effects even at a low dose and dose rate. The possibility of electronic energy loss playing a role in the present context has been discussed but further work would be required to clarify this issue. Meanwhile, the large hardness changes that have been achieved demonstrate the potential of high energy heavy ion irradiation in improving the properties of relatively thick films.

References