Conf-950201--4

LA-UR- 95- 341

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Submitted to: TMS Annual Meeting

February 12-16, 1995
Las Vegas, Nevada

MASTER

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Plasma Source Ion Implantation of Ammonia Into Electroplated Chromium

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Abstract

Ammonia gas (NH_3) has been used as a nitrogen source for plasma source ion implantation processing of electroplated chromium. No evidence was found of increased hydrogen concentrations in the bulk material, implying that ammonia can be used without risking hydrogen embrittlement. The retained nitrogen dose of 2.1×10^{17} N-at/cm^2 is sufficient to increase the surface hardness of electroplated Cr by 24% and decrease the wear rate by a factor of 4.

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Introduction

U.S. industry currently uses wet chemical baths to produce protective chrome layers on process equipment to enhance wear and corrosion resistance. Currently, environmental regulations are increasing the cost of chrome electroplating. An environmentally acceptable technology which would reduce or eliminate the need for chrome plating would not only benefit the environment, but would also strengthen U.S. industrial competitiveness.

Nitrogen ion implantation of chromium has demonstrated the ability to dramatically increase the surface hardness and decrease the wear rate[1-13]. As shown in Fig. 1, implantation of nitrogen ions into a draw die, electroplated with Cr, dramatically increases the field tested service life[14]. It is thus possible that nitrogen implantation could increase the service life of electroplated chromium resulting in waste stream reduction. Advantages of ion implantation over other surface modification techniques include its ability to provide implanted atomic concentrations above limits imposed by chemical solubility at low temperature without causing dimensional changes.

However, conventional beamline implantation requires expensive particle accelerators, magnetic mass filtering, beam rastering, beam masking and target manipulation. In addition, implantation of geometrically complicated surfaces requiring target manipulation is especially difficult for large and/or heavy components.

Plasma Source Ion Implantation (PSII), is a non-line of sight technique capable of producing a more economical, uniform and effective implant[15]. PSII can extend chrome plating lifetime thereby reducing the demand, and concomitantly reducing the waste stream. In certain applications PSII can replace hard chrome plating by producing a low-friction, high-strength, corrosion resistant surface on the uncoated base material. A recent cost study has shown that PSII can be an order of magnitude less expensive than present low current beamline implantation [16].

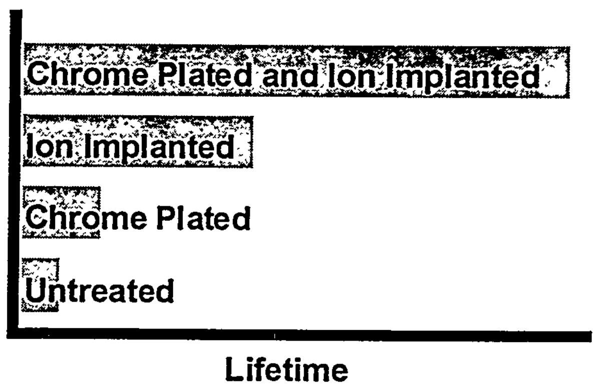

Figure 1. Ion implantation dramatically improves the wear lifetime of a chrome plated industrial steel draw die [14].

In this paper results are presented for nitrogen PSII of electroplated chromium. The implantation is performed using an ammonia plasma. The characterization of implanted samples includes high energy resonant ion back-scattering, nanoindentation, pin-on-disk wear testing, and numerical calculation of the implanted profile using TAMIX. From analysis of these results, the suitability of ammonia PSII to increase the wear life of electroplated chromium is determined and suggestions for optimizing ammonia PSII processing are made.

Plasma Source Ion Implantation

In PSII, the target to be implanted is immersed in a plasma and repetitively pulsed to a high negative voltage (see Fig. 2). An expanding boundary layer (sheath) forms around the target during the voltage pulse. The electric field within this expanding sheath accelerates ions toward all target surfaces

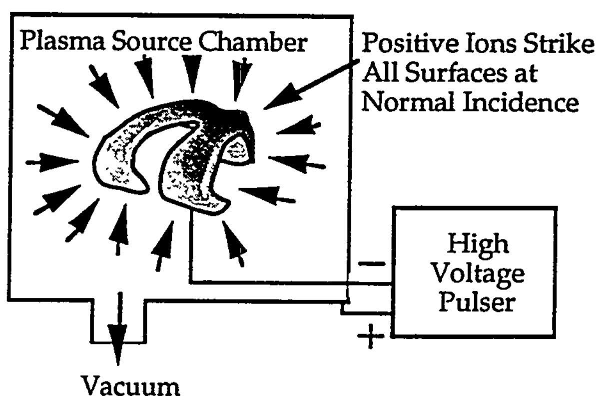

Figure 2. Schematic of the non-line of sight, Plasma Source Ion Implantation process.

simultaneously, eliminating the need for target manipulation or masking. This allows a more uniform implant [17], and it also allows the treatment of a variety of shapes without a complex refixturing effort.

The ultimate sheath extent (and the conformality of the resulting implant) depends on several parameters [18-19]. The expansion rate varies directly with target voltage and inversely with plasma density and ion mass. Since the voltage and ion species are usually fixed by materials considerations, plasma density adjustments are made to control the sheath expansion.

There are several constraints on the size of the expanding sheath formed during pulsed implantation. The final sheath extent should be small enough that it does not intersect the vacuum chamber walls, which could result in loss of implant uniformity. Similarly, in batch implantation, the sheaths from neighboring targets should remain separate. Another consideration is that of collisionality. Ions traversing the sheath can collide with neutral gas molecules and lose energy, lowering the effectiveness of the implant. The sheath dimension should be kept less than the collision mean-free path.

The issue of sheath conformality must be addressed. If the sheath is allowed to grow large compared with the features of the component to be implanted, the conformality and resulting uniformity and retained dose will be compromised. Finally, the pulse repetition frequency must be kept low enough to allow the plasma sufficient time to fill in the sheath following the high voltage pulse [20].

The amount of current collected during the voltage pulse increases with both plasma density and target area. The collected current is limited by the capability of the pulse modulator. For a given target area, this current limit determines the maximum allowable plasma density and therefore the resulting sheath conformality.

For large area implants, a modulator must be chosen with a high peak current capability, since a large current is collected during the voltage rise. If the peak current limit is too low, a large area implant must be performed at low plasma density, resulting in a large sheath and poor implant uniformity. If the current limit is such that the sheath is larger than the vacuum chamber dimensions, there will be no window in which to operate.

Experimental setup

The implantation was performed in the Los Alamos National Laboratory large scale PSII facility [21]. Chromium was electro-deposited on stainless steel samples. Following plating, the samples were diamond polished to an arithmetic roughness of 0.2 μm. The samples were then placed on a 60x10x2 cm water cooled target stage and immersed in a 0.3 mTorr, 200 W, capacitively coupled rf, ammonia plasma. The target was biased to -60 kV for 20 μs pulses applied at 400 Hz. The peak current collected during the pulse was 25 A.

Ammonia (NH_3) was chosen to maximize the implantation depth. The negative, high voltage pulse applied to the target attracts all positively charged ions that appear within the ultimate sheath extent. In a nitrogen plasma, these ions could be molecular (N_2^+) or atomic (N^+). For a 60 kV implant, both types of ions will be accelerated through the sheath to the same (60 keV) energy. However, upon impact with the surface the N_2^+ ion will dissociate into two 30 keV ions. These low energy ions result in a shallow implant, surface sputtering, low retained dose, and in some cases an unacceptable implant. It was hoped that the use of ammonia as the precursor gas would result in a higher fraction of atomic ions (N^+). Implantation of ammonia ions (NH_3^+) at 60 keV will result in a 49 keV nitrogen ion upon impact with the surface.

The estimated incident dose was 1.4×10^{18} ions/cm^2. This ion dose was most likely made up of a wide variety of ions (nitrogen, hydrogen and combinations of nitrogen and hydrogen) due to the dissociation of the ammonia gas. A concern for ammonia implantation of Cr is hydrogen embrittlement of the Cr layer.

High energy resonant ion back-scattering (HERBS) to determine the retained nitrogen dose was accomplished using a 28 nA, 8.9 MeV alpha particle beam at normal incidence with 20 μC of collected charge, and 166° scattering angle. These conditions take advantage of the 75x increase in nitrogen sensitivity attained when using a 8.9 MeV alpha particle beam [22]. Elastic Recoil Detection (ERD) analysis, to determine the hydrogen concentration, was achieved using a 3.55 MeV alpha particle beam incident on the surface at 75° with a scattering angle of 30°, beam current of 23 nA and 12 μC of collected charge.

Nanoindentation tests were performed using a Nano Indenter® II manufactured by NanoInstruments, Inc., Knoxville, TN. The hardness and elastic modulus of the implanted and unimplanted samples was calculated (including elastic corrections) from load/displacement curves at eight depths. Average values and standard deviations were calculated from eight measurements of hardness and elastic modulus at each depth.

Unlubricated pin-on-disk (POD) tribological tests were conducted using a 6 mm diameter ruby (Al_2O_3:Cr) ball, a load of 1.2 N, in air and at 50% relative humidity. The contact stress was 1.6 GPa, which is significantly less than the yield stress of 8 GPa for electrodeposited Cr. The track diameter was about 3.5 mm, the sliding speed was ~26 mm/sec, and the total sliding distance was ~310 meters. After testing, the maximum width of the wear track was determined using optical microscopy. Since the Cr-plated surface was too rough for surface profilometry, the wear track was assumed to mirror the profile of the ruby ball. Assuming the wear track was in the shape of a segment of a circle, the wear track volume, and subsequently the wear rate [23], were calculated from the width of the wear track.

Results and Analysis

HERBS measurements indicated a retained nitrogen dose of 2.1±0.2 x10^{17} N-at/cm^2 and a retained hydrogen dose of 0.5±0.05 x10^{17} H-at/cm^2. The modified surface layer consists of 45 at% Cr, 10 at% H and 45 at% N. No evidence of an increase in the bulk hydrogen concentration (0.3 at%), beyond the implanted surface layer, was found.

Nanohardness tests indicated a 24% increase of the surface hardness after nitrogen ion implantation. The hardness as a function of depth is shown in Fig. 4. The hardness increase is consistent with that reported in the literature for implantation of 49 keV nitrogen to a dose of

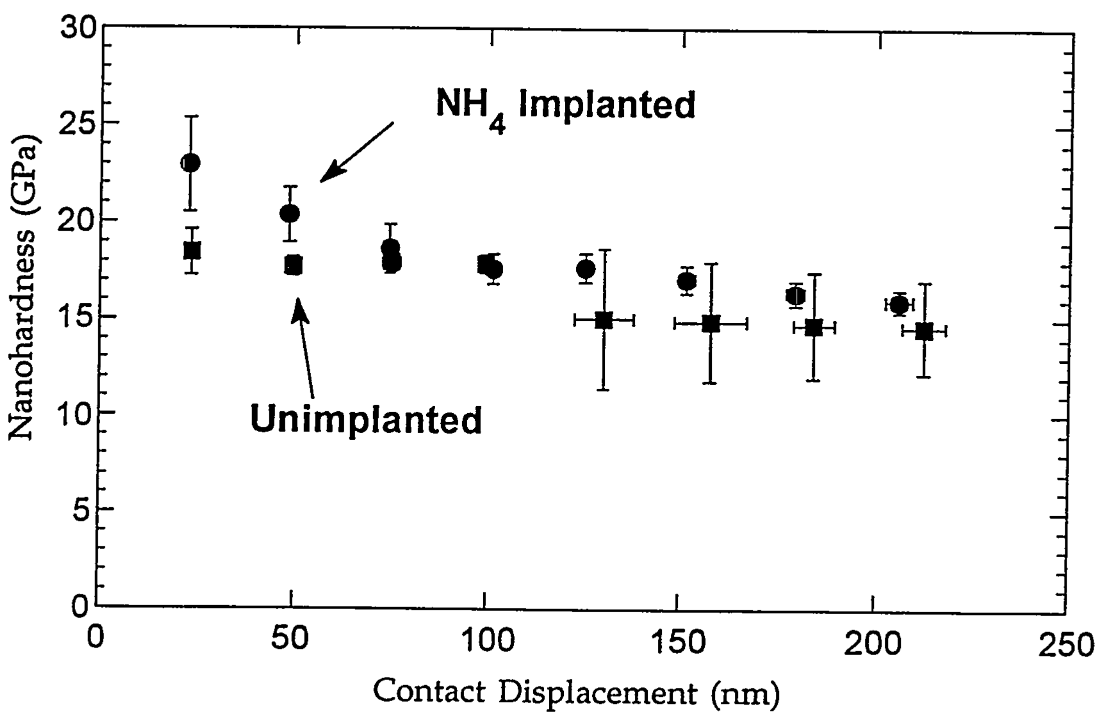

Figure 4. Hardness as a function of contact displacement for unimplanted and ammonia implanted Cr plating as determined by nanoindentation tests.

2.1×10^{17} cm^{-2}. POD wear tests have indicated the increased surface hardness results in a reduction in the wear rate by a factor of four (Fig. 5). Under these tribological conditions, there is no significant decrease in the coefficient of friction accompanying the decrease in the wear rate.

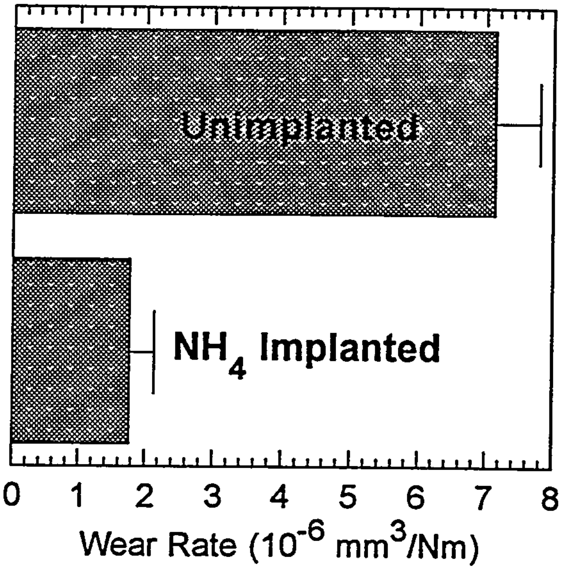

Figure 5. Pin-on-disk wear tests of unimplanted and ammonia implanted Cr plating indicate a reduction in the wear rate by a factor of four. Error bars are shown on right.

In order to resolve the large discrepancy between the incident and retained nitrogen dose, ion-target interaction modeling was performed using the TAMIX code[24]. TAMIX is a model which calculates the retained dose and surface recession for a given target material, incident dose, ion species, and distributions of ion energy and incident angle.

A model of sheath propagation and current collection [19] was used to estimate the sheath size during the implant. The model input plasma density was varied until the predicted current collection (for an emission coefficient of 8.5 at 60 keV) matched that measured during the implant. The plasma density which resulted in a match was 6×10^{8} cm^{-3} which results in a predicted sheath radius of 31 cm from the center of the target. From this prediction it is evident that the sheath is by no means conformal to the target and is very nearly cylindrical in shape. It was therefore estimated that ions from all angles up to about 70° from normal incidence were included in the collected current. In performing preliminary TAMIX runs, it was found that the predicted implant profile was much less dependent on energy spectrum than on angle spectrum. Since TAMIX only allows 10 total angles and energies it was decided to include only an angle distribution and ignore the low energy tail inherent in PSII. From the measured voltage and current waveforms, it was estimated that 60% of the ions were collected at full energy.

Using the above information, a TAMIX run was performed for a 49 keV nitrogen implant with an incident dose of 1.4×10^{18} at/cm^2 on a Cr target. The angle spectrum used was uniform up to 70° from the normal with no ions at angles greater than 70°. TAMIX gives retained dose of $2.7 \pm 0.6 \times 10^{17}$ N-at/cm^2 which compares favorably to the measured retained dose of 2.1×10^{17} N-at/cm^2. The 20% error in the predicted dose is due to the uncertainty in the density of the electroplated Cr layer. A higher retained dose could be achieved with a more conformal implant. A dramatically thinner sheath (< 10 cm) would give angles of incidence nearer to the surface normal giving a higher retained dose. Such an implant requires a high plasma density ($>10^{11}$ cm^3) with a very high peak current (>200 A) modulator. These requirements are beyond the capability of our present system.

Conclusions

This work has shown that ammonia gas (NH_3) can be used as a nitrogen source for PSII processing of electroplated chromium. Since there is no evidence of increased hydrogen concentrations in the bulk material, it seems likely that ammonia can be used for PSII processes without risking hydrogen embrittlement. In addition, we have seen that a retained nitrogen dose of 2.1×10^{17} N-at/cm^2 is sufficient to increase the surface hardness of electroplated Cr by 24% and decrease the wear rate by a factor of 4. While the implantation conditions used yielded a less than optimum retained dose due to large sheaths and shallow incidence angle resulting from low peak currents, the resulting decrease in wear rate could be satisfactory for many applications.

Acknowledgments

The authors would like to thank William Horne of Empire Hard Chrome, Chicago, IL for supplying the electroplated Cr samples for implantation, NanoInstruments, Inc. for the nanohardness results, and the Ion Beam Materials Laboratory, Los Alamos National Laboratory for assistance with the ion beam analysis. This work was supported by the US Department of Energy.

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