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Surface hardness improvement by dynamic recoil implantation

I. N. EVDOKIMOV,* G. FISCHER†
Department of Electrical Engineering, University of Salford, Salford M5 4WT, UK

Substantial increase of mild steel hardness is achieved by a novel recoil implantation technique. The technique is described and the results are analysed in view of the effects of radiation damage and the implant's concentration profile.

1. Introduction

Ion implantation for the purpose of changing the physical and chemical properties of the solids has been extensively investigated over the past decade [1, 2]. The word "ion" is used to distinguish this method from other doping techniques as it normally requires preliminary ionization of the dopant atoms which are subsequently accelerated, mass analysed and focused into an ion beam which is directed onto the treated surface. In this way a desired chemical composition and a well-defined dopant profile are achieved. At the same time such treatment results in a substantial loss of initial ion current, severely limiting the ion dose rate. Furthermore the creation of ions of dopant materials which normally exist in the solid phase, such as most metals, is still a serious technological problem because of the difficulties connected with their vaporization or the low ionization rates.

With respect to the conventional ion implantation the comparatively new method of recoil implantation [3] provides a lot of advantages in cases where only a very shallow near surface layer has to be implanted. This method consists of the deposition of the dopant material onto the substrate's surface and a subsequent bombardment by energetic (usually inert gas) ions which knock dopant atoms into the substrate. As the ionization of the dopant material is not required, higher primary ion beam densities and thus larger dopant concentrations can be achieved. The dopant film on the implanted surface can be produced by any convenient technique such as thermal evaporation or sputtering. Various theoretical and technological aspects of recoil implantation have been explored recently [4–6] by different workers. It is now realized that this method is potentially very promising especially in cases when volume or thick layer doping is not required such as in production of solar cells, Schottky diodes, catalysts, altering surface mechanical properties, corrosion protection, etc. At the same time, a serious drawback of this method is now realized. It is the limitation of dopant concentration due to unavoidable resputtering of the implanted layer caused by a primary ion beam.

This technological limitation can be removed by a novel technique called dynamic recoil implantation (DRI) [7, 8]. Here a constant balance is maintained between the resputtering rate and a continuous influx of the dopant material during the process of surface treatment. In this way very high surface dopant concentrations may be achieved which cannot be reached by other implantation techniques.

In spite of its advantages, DRI method has not yet been used for any technologically important applications. The subject of the present paper is the study of DRI effect on surface hardness of mild steel with nickel used as a dopant material. Comparatively low, easily produced acceleration voltages (up to 20 keV) were utilized, because, in the case of conventional direct ion implantation there is already some evidence that surface hardness can be altered by low energy implants [2].

*Permanent address: Physics Department, I. M. Gubkin's Institute for Oil and Gas Industry, Leninsky Prospekt 65 Moscow, 117296 USSR.
†Present address: Department of Engineering Physics, McMaster University, Hamilton, Ontario L8X 4M1, Canada.

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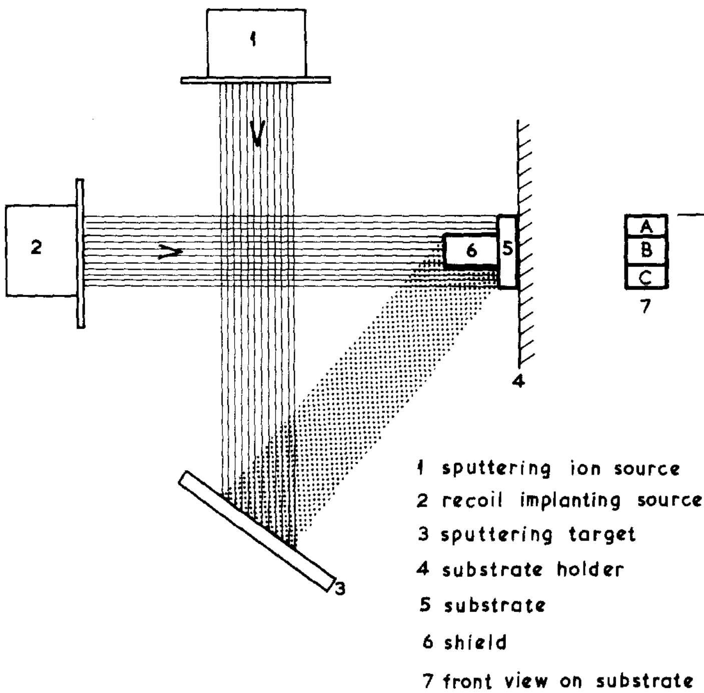

Figure 1 Schematic diagram of the experimental arrangement.

2. Experimental procedure

Because the DRI method and apparatus used here are described in detail elsewhere [8] only a short description of the process is given here. A schematic diagram of the apparatus is shown in Fig. 1. The implanting ion source [2] is a high energy (max. ~ 25 keV), low intensity ($\sim 5\,\mu$A cm^{-2}) narrow beam source. The nickel atoms are deposited onto the steel substrate [5] by sputtering a high purity (99.99+%) auxiliary target [3] with a high intensity (~ 1 mA cm^{-2}) low energy (~ 2.5 keV) ion beam produced by a specially designed [9] sputtering source [1]. Argon was used as a support gas for both sources because it gives satisfactory high sputtering yields, is relatively inexpensive and easy to obtain. The sputtering target and a substrate are placed in a vacuum chamber evacuated by a high speed pumping system. The implanting ion beam current (and ion dose) was determined with a Faraday cup which could be moved in front of the substrate. The balance between dopant deposition and resputtering was achieved by altering the ratio of the implanting and sputtering ion beam currents. The state of balance is detected by a quartz crystal oscillator microbalance. The constancy of the oscillator frequency indicates that the mass loading of the crystal is constant, i.e. the deposited and resputtered masses are equal for any time interval. The same quartz crystal was used to measure the initial film thickness deposited prior to the recoil implantation treatment.

The optimum dopant film thickness, which is to be maintained during the DRI treatment, is defined by the requirement of maximum recoil implantation yield. This is achieved if the dopant layer thickness is close to the mean damage depth of the implanting ion species, i.e. if the maximum energy deposition of these ions occurs near the interface between the dopant film and the substrate [10]. For 20 keV Ar^+ implanting ions, the optimum Ni film thickness was calculated to be ~ 50 Å. A standard bombarding ion dose to 10^{16} Ar^+ ions per cm^2 was used in all the experiments.

For implantation, 15 mm x 10 mm x 3 mm samples were cut from a sheet of mild steel (type BS1449). All samples were mechanically polished to mirror finish. The strain caused by mechanical treatment, was removed by prolonged vibratory polishing with fine 0.05 μm alumina powder. Subsequent measurements showed that this vibratory polishing treatment notably decreased the statistical fluctuations in the results.

During implantation, the surface of these samples was divided into three approximately equal areas (5 mm x 10 mm) by a special shield (item 6, Fig. 1). As can be seen from Fig. 1, part C undergoes the complete DRI treatment, part B is covered by the shield and remains untreated, and part A is shielded from the influx of the dopant but is exposed to the implanting Ar^+ beam. This arrangement makes it possible to investigate the effect of the radiation damage on the implanted samples and to reduce the experimental error by relating any systematic changes to the original parameters.

Microhardness measurements were performed on a conventional hardness tester with a Knoop diamond indenter. Loads of 5 and 10 g were used to enhance the sensitivity of measurements to hardness changes in the extreme surface layer.

3. Results

On all the samples, both implanted and untreated, the presence of microconstituents with substantially different hardness was observed. Their average size was about 10 to 50 μm and in some cases they led to the distortion of the indenter imprint. The nature of these microconstituents was not investigated. A plausible cause is the particles of cementite and complex carbides present in commercial steels [11]. Imprints distorted by these phases were not taken into consideration.

Due to the time lag between the implantation and the hardness measurements it was necessary to check the possible influence of oxidation and recovery in the implanted layer. The measurements showed no noticeable change in the microhardness between 0.5 h and two weeks after the DRI treatment.

A typical set of experimental results obtained from vibratory polished samples is shown in Fig. 2. A reproducible increase of about 30 to 35% in the surface hardness is found on surface areas (C), subjected to the DRI. On areas (A) bombarded only by 20 keV Ar^+ beam no reliable hardness changes could be detected since both increase and decrease of hardness was observed within the range of statistical fluctuations.

On mechanically polished surfaces qualitatively the same effect was observed, i.e., a notable increase in hardness on DRI treated areas and no reproduceable change on Ar^+ bombarded ones. In this case, however, the standard deviation of the results over the sample's surface was much larger.

Measurements were carried out also to establish the influence of the residual Ni film left on the surface after implantation. From hardness measurements on unimplanted samples with a Ni layer on the surface it could be concluded that in our experimental conditions this film had no influence on surface hardness. The standard deviation in these measurements depended on whether or not the sample surface was Ar^+ bombarded prior to Ni deposition. The error margin was between 20 and 25% for the unbombarded samples and it decreased to between 8 and 10% for the prebombarded ones. A probable explanation is the greater uniformity of Ni film deposited on the surface cleaned by the Ar^+ beam.

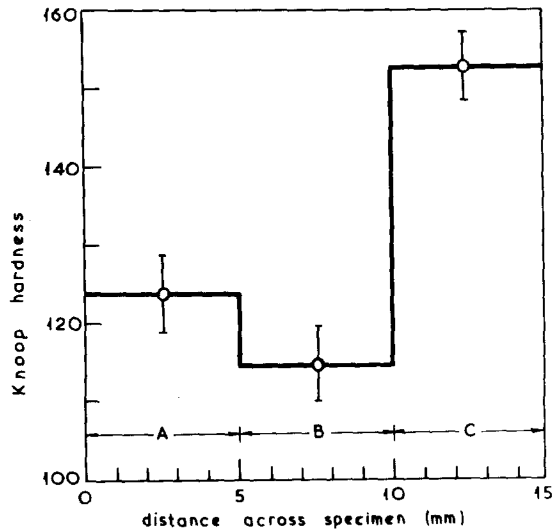

Figure 2 The microhardness scan across the substrate's surface.

4. Discussion

Summarizing the results presented here, we may conclude that the DRI is an effective tool for the modification of the surface hardness.

As for the possible mechanisms of the obtained hardness improvement, two main effects [2, 12] should be taken into account. The first is the result of the radiation damage induced by bombarding ions and recoils into the crystal lattice of the substrate. This can result in dislocation pinning etc., thus increasing the yield stress, σ, of the bombarded material. This leads to an increase in the hardness, H, as these quantities are linearly related, i.e. $H = C\sigma$, where C is a constant.

It has been shown [13] that for metals, bombarded with medium energy (keV) Ar^+ ions, the characteristic temperature of Ar desorption from the surface is usually not lower than 500 to 600 K. Consequently, irradiation at room temperature, as in the present case, leads to an accumulation of Ar atoms in the target, further increasing the number of defects.

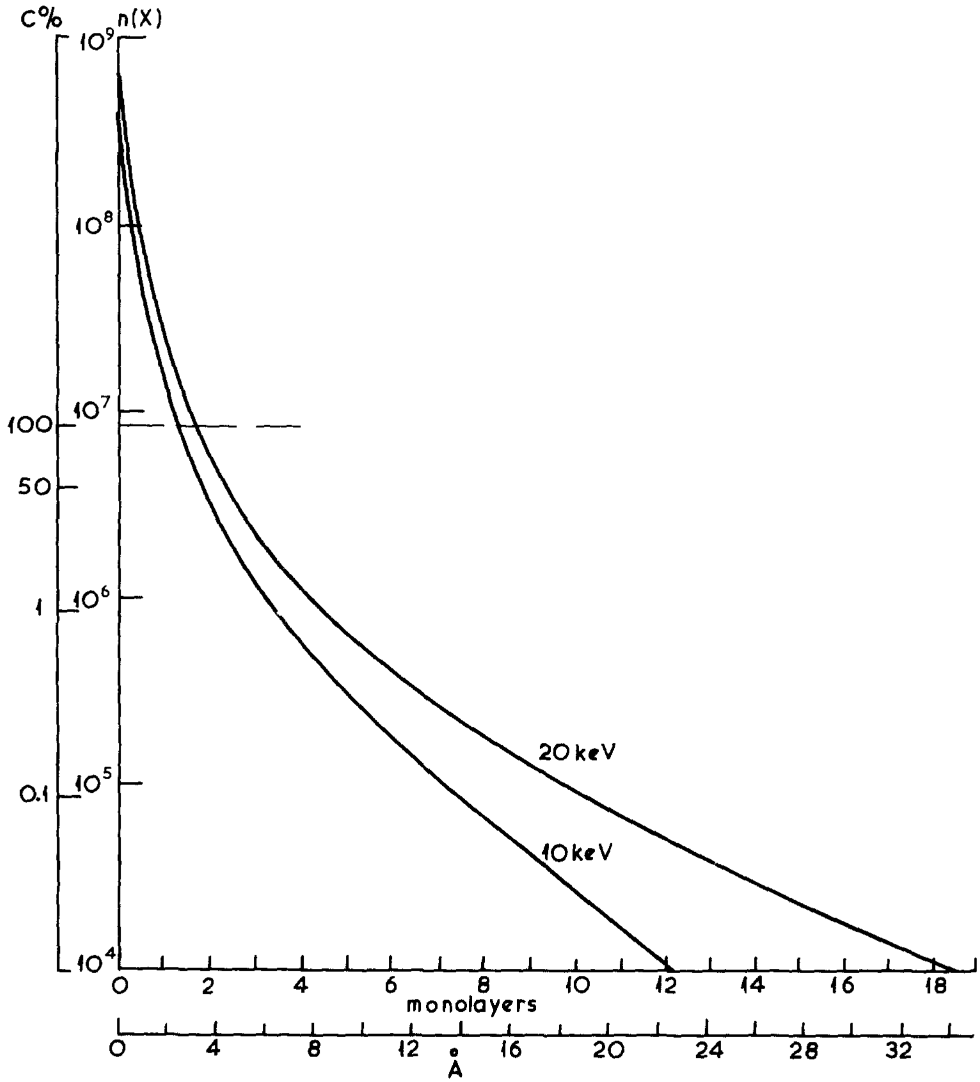

Figure 3 Calculated depth profiles of implanted Ni. Scales for both concentrations (C) and the number of implanted atoms (n) are shown.

Existing experimental data, concerning the influence of noble gas ions bombardment on surface hardness, are contradictory. In [14], in agreement with our results, no noticeable hardness change was observed after Ar^+ bombardment. On the contrary, large hardness increase (up to 50%) was described in [15]. The discrepency of our results with those of Pavlov *et al.* [15] can be attributed to the dependence of hardness on the bombarding ion dose. In [15] the hardness was nearly constant up to a dose of $\sim 2 \times 10^{17}$ cm^{-2}. At higher doses an increase in hardness occurred up to a saturation at a dose of $\sim 10^{18}$ cm^{-2}. This dependence can be associated with the formation of complex defect conglomerates, such as gas bubbles etc., at high doses [16]. At lower doses up to $\sim 10^{16}$ cm^{-2} as in our case, mainly point defects or simple clusters are formed, which obviously have less influence on surface hardness.

With the direct effect of radiation disorder induced into the substrate's lattice excluded, the cause of the observed hardness increase should lie in the specific properties of Ni implant interaction with the steel matrix. In order to give a detailed description of implanted samples, the Ni depth distribution should be estimated. The experimental evaluation of the depth profile is complicated because of the very small implantation depth (which exclude sectioning techniques) and the closeness of the dopant and substrate atomic masses (preventing the use of profiling with the help of Rutherford backscattering). The results of theoretical calculation of depth profile are shown in Fig. 3. The calculations were carried out by the method developed in [10]. In order to demonstrate the effect of energy dopant film thickness optimization two profiles are presented. Both profiles are calculated for the same balance thickness of ~ 50 Å. It can be seen that in optimum case (20 keV) much higher dopant concentrations are achieved. As there is no built in concentration limitation in the theory, non-physical values are obtained in the immediate vicinity of the interface (concentrations far exceeding 100%). In reality it means that most of the substrate material is removed from that region (the first two to three monolayers) and is substituted by the dopant. Although this concentration profile will be subjected to radiation-induced and thermal diffusion, its basic features, i.e. the very high surface concentration and the steeply falling tail, will remain. The mutual diffusion of Ni and Fe atoms is expected to increase the thickness of the near-surface layer with comparable partial concentrations of both components. This layer is supposed to provide improved corrosion resistance, characteristic of the rich Ni–Fe alloys [17]. Deeper lying substrate layers with smaller Ni concentration (less than a few atomic per cent) are believed to be responsible for the observed increase in surface hardness. It is known [18] that in low concentrations alloy-forming or chemically active impurities may greatly enhance vacancy loop and void formation by nucleating primary vacancies formed in the displacement cascade. Thus the role of Ni dopant in DRI hardness improvement is seen as two-fold. Energetic Ni knock-on atoms both produce radiation defects in the substrate lattice (together with the primary Ar^+ ions) and subsequently assist in the formation of defect agglomerates.

5. Conclusion

The dynamic recoil implantation method is known to have certain technological advantages with respect to other ion implantation techniques. The experimental results show that it can be also effectively used for improving surface mechanical properties. An increase of surface hardness of about 30 to 35% can be achieved for commercial mild steel implanted with nickel. Analysis of the nature of this effect indicates that in hardness improvement complex defect clusters play the major role. As a by-product of this treatment improved corrosion resistance may be also achieved.

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