



TEM INVESTIGATIONS OF DAMAGE STRUCTURE OF PURE GOLD AFTER NITROGEN PLASMA IMMERSION ION IMPLANTATION (PIII) USING RF DISCHARGES

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Abstract

The paper presents experimental results concerning microstructural changes caused by PIII. Thus, the main aim of these experiments was to make preliminary investigations of structural damage introduced by N^+ PIII into gold in such circumstances where precipitation processes are not available and structural damage only exists. After electropolishing Au foils with a [100] preferred orientation were PIII implanted to a total dose of $2 \times 10^{17} N^+$ ions/cm². Gold was used in the present study for three reasons: first, the noble character of gold will minimize contamination problems, second, thus far there are no definite evidence about gold nitride formation even when the dose was as high as $2 \times 10^{18} N^+$ /cm², and third, theoretical calculations give for this metal the highest interstitial and substitutional solubility. It has been observed that pure gold after nitrogen PIII contains a great deal of small gas bubbles. These bubbles can grow as a result of their migration, consequent collision and coalescence. It may be assumed that bubble creation, migration, coalescence and growth can best be reduced by the introduction of stable precipitates into the metal.

Keywords: *plasma immersion ion implantation, damage structure*

1. Physical aspects of ion - surface interaction

An ion of energy greater than a few keV striking a solid surface at normal incidence has a probability approaching unity, of entering that surface.

On its way to its final resting place however, the incoming particle will lose typically 70% of its energy in a series of collisions with lattice atoms. If such atoms receive energy greater than a threshold displacement energy E_d of order 20-50 eV they will be recoiled from their normal lattice site to leave a vacancy at their original position and form an interstitial elsewhere.

When the energy transfer is large, these displaced atoms can cause further displacements to form a cascade of recoils. The cascade mechanism depends mainly on the nature of the metal, the bombarding particle and the energy, but is relatively insensitive to other factors if the temperature is below that at which clusters are stable [5,25].

The situation is far removed from that found in conditions of thermal equilibrium. Since the incorporation of a foreign species into a solid by ion implantation is not constrained by equilibrium

considerations, non-conventional near-surface alloys can be formed [22,23].

Seeger first reviewed the nature of a displacement cascade (DC) in irradiated crystalline materials and the concepts of displacement spikes, replacement collision sequences (RCS), "diluted" or depleted zones, and thermal spikes which are all individual aspects of a DC [18].

The ideas embodied in Fig. 1 are still qualitatively correct, and they have allowed researches to understand many of the effects of DC on properties.

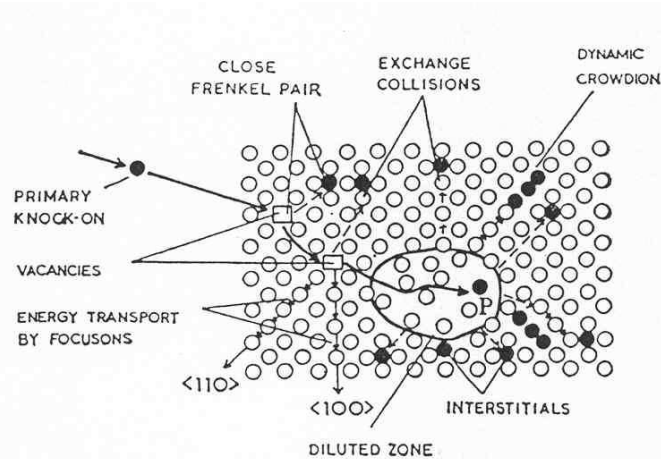


Fig. 1. Schematic two-dimensional representation of the depleted zone and its environment in a face-centred cubic crystal. A primary knock-on impinges from the left and comes to rest on the site P [18]

The core of a DC is void-like in nature, and the missing atoms (self-interstitial atoms (SIA)) reside on the periphery of the DC. This was supported by the results of Calder et al [4] who observed that loops in gold were only formed in the core of cascades in the thermal spike phase (10^{-11} - 10^{-12} s) of cascade evolution. Since in cascades which do collapse, most vacancies retained in the resulting loops, thereby suggesting that interstitials were effectively separated from vacancies in the collision phase of cascade formation. It was found that collapse occurs even at 4.2K and must therefore take place in the thermal spike phase. To the same conclusion came Jäger et al [2,11] who found that vacancy clusters in gold formed as the dominant cluster type as a result of vacancy rearrangements in depleted zones, both in individual cascades and after cascade overlap at higher doses.

Displacement spike is a very large numbers of atoms displaced in a small volume of material. There is possible to focus energy along close-packed crystallographic directions in a crystalline material, this phenomenon is called a focuson. The focusons along the [110] directions in a f.c.c. lattice could lead to the production of what Seeger termed, "dynamic crowdions". When a "dynamic crowdion" rins out of energy an SIA is deposited at the end of the track, thus creating a Frenkel pair with a large separation between the vacancy and the SIA. It is now common to call a "dynamic crowdion", a replacement collision sequence (RCS) [19]. The region denoted as the "diluted zone" is now called a DC.

This vacancy rich core in the ion track may subsequently collapse to form a vacancy dislocation loop. Experiments have shown that, in many cases, the vacancy rich regions collapse within the cooling phase of the cascade to form vacancy dislocations loops [4,19]. They are usually Frank loops on (111) habit planes, with $b = a/3$ (111) [11,19].

The mechanisms which lead to recovery by collapse are not yet understood, but their importance is undoubted because they provide a means by which the vacancy component of implantation damage is retained within the microstructure [4]. Likewise the interstitials can migrate to form interstitials loops [5]. Under such conditions, conventional metallurgical phase relations can be violated as shown by Marwick et al [15].

All these processes occur within about 10^{-11} - 10^{-12} s from the impact of the ion. There is thus a

short lived hot spike of material which can promote so-called radiation induced segregation as seen by Marwick et al above [15], or, can encourage diffusion to form equilibrium phases, the process being referred to as radiation enhanced diffusion within the volume of the DC [19].

However, only heavy ions deposit enough energy in the stopping volume to produce a "depleted zone" and hence lattice collapse into a vacancy cluster. When the damage density is lower (light ions), the local vacancy density is insufficient to produce a vacancy cluster [17]. Thermally activated mobile interstitials may, however, form interstitial clusters. Thus, the nature of the defect clusters depends on the mass and energy of the incoming ion [17]. Generally at implantation energies of 50-150 keV, the nature of observed defect clusters depends on the mass of the implanted ion: light ion (atomic number A below 85) irradiations created interstitial loops, while heavier ion implantation created vacancy loops [17].

Transmission electron microscopy (TEM) may be used successfully to characterize stable defect-cluster configurations resulting from energetic displacement cascade damage in metals and to determination of the phase composition after ion implantation. The objective of such studies is, besides fundamental aspects, an understanding of defect production during neutron irradiation in reactor materials and of modifications in structure and composition of materials by ion implantation.

2. Structural changes and depth profile of implanted layer

Ion implantation possesses several distinct advantages over other techniques for the surface treatment of materials. These are:

1. The ability to introduce any ion into the surface region of any substrate without the constraints of thermodynamic phase equilibrium. The optimum effects were obtained by nitrogen implantation with energies of 40-80 keV and optimum ion dose was found at $4-8 \times 10^{17}$ ions/cm².

Lower doses produce no visible effect and higher doses sometimes result in a change of the initial state for the worse. The implanted layer only reaches a thickness of about 100-200 nm but the effect often considerably exceeds this range.

The thickness of a developed dislocation structure in the near-surface layer exceeds the ion range by several orders of magnitude. The thickness of the layer with developed dislocation structure was found greater than 100 μm .

2. The ability to perform the implantation at a low process temperature. But it is ineffective for all applications involving high process temperatures. This is because of the instability at higher temperatures of the nitrogen induced defects and precipitates formed in the surface layer during implantation which are thought to be responsible for the beneficial influence.

3. The ability to perform the treatment without further need of annealing or refinishing.

4. The absence of coating adhesion problems.

The implantation depth decreases with increasing ion mass and increasing the energy results in an increase of the penetration depth.

It is known that particle implantation causes damage in crystals which appears on the transmission micrographs in general as "black dots" or "black spots" with diameters $d \leq 100 \text{ \AA}$, i.e. small compared with the extinction length $\zeta_{\mathbf{g}}$ of the operating diffraction vector \mathbf{g} .

The sputtering factors for Cu, Ag and Au are high and the saturation values remain low, which, in turn, means that no blister formation can occur [1,25]. However, if higher bombarding energies were used, the blister formation could also occur in Cu, Ag, Au elements [13], and the number of blisters was evidently proportional to the range of the implanted ions. Accordingly, if no nitrogen migration occurs during treatment, with its relatively low solubility, the nitrogen dose should be selected precisely to avoid blister formation [1,13,25].

3. Precipitation processes in implanted materials

Ion implantation is a non equilibrium process. There is possible to implant materials with impurities to concentration levels which far exceed the solid solubility. The return of the system to thermodynamic equilibrium is often accomplished by precipitation of the implanted species or a compound involving atoms of both the host and the implanted species. This process may involve very long time scales when taking place at room temperature or it may take place dynamically during the implantation.

Precipitates which are formed during implantation depend on the alloying elements. The kind of nitride produced depends of course on the different affinities of the alloying elements for nitrogen.

Ion implantation with interstitial species, such as nitrogen, can have a major influence on surface related mechanical properties in a wide range of ferrous alloys. The formation of numerous small sized precipitates, high densities of dislocations and martensitic transformation are supposed to be favorable factors for hardening the outermost layer.

Many metal nitrides, such as TiN, ZrN etc., belong to the category of easily produced nitrides [12,20]. However, noble metal nitrides are difficult to form or even not obtainable under implantation conditions. In recent years, AgN₃ and CuN₃ phases were observed by TEM pattern after implantation to a dose 2×10^{18} Ncm⁻² [17]. Yet, for nitrogen implantation into Au films, no definite evidence was obtained about gold nitride formation even when the dose was high as 2×10^{18} N cm⁻² [38]. Kelly [12,20] suggested, that failing to appear of gold nitride could be explained by N loss at the surface.

Anttila [1,24] attributed the failure of the formation of noble metal nitride to the high sputtering yield of nitrogen ion-noble metal partners, which prevented the average nitrogen concentration in the implanted layer from reaching the required stoichiometry. Surface recession due to sputtering seems to be played important role on nitride formation but it needs further study.

Yet, the precipitated phases can have an effect on the actual shape of the implantation profiles. It was found that second phase precipitation however does not affect the total retained dose of the implanted species very much since the precipitated region is away from the surface and the loss due to sputtering is not modified. The effects become more significant if the implanted species are highly mobile during the implantation process.

4. Plasma immersion ion implantation (PIII)

Conventional ion implantation is a line-of-sight process in which ions are extracted from an ion source, accelerated as a directed beam to high energy and then raster scanned across the target. If the target is nonplanar, target manipulation is required to implant all sides of the target. The necessary target manipulation adds complexity and reduces the size of the target which can be implanted.

Thus, the main disadvantages are the relatively high process costs and the restriction to visible areas because it is a line-of-sight process. This precludes ion implantation treatment of parts with obscured or re-entrant features.

These all disadvantages are overcome in a new technique for the ion implantation of materials which has been reported by Conrad et al. [2,3,6,7,8], Tendys et al. [14,21], and Hossary et al. [9]. This technique has been named plasma immersion ion implantation (PIII or PI³), or plasma source ion implantation (PSII). PIII is a non-line-of-sight technique [6,10]. In PIII, the target is placed directly in plasma source and pulsed to high negative potential relative to the chamber walls. Ions are accelerated normal to the target surface, across the plasma sheath, thus eliminating not only the line-of-sight problems of conventional ion implantation but also the retained dose problem. The pulse amplitude, width and spacing are independently and continuously variable. The temperature

of the sample can be controlled by using a pulsed discharge which can be varied in both frequency and amplitude [9]. All advantages of PIII over conventional ion implantation have been discussed widely by Conrad et al. [6,10].

Up to now any experimental results have not been published concerning microstructural changes caused by PIII. Thus, the main aim of these experiments was to make preliminary investigations of structural damage introduced by N^+ PIII into gold in situation where precipitation processes are not available and structural damage only exists.

5. Experimental procedures

Air-cleaved NaCl (100) surfaces were used as substrates, heated at 450°C on Mo resistively heated strip. NaCl was cleaved immediately before loading into the vacuum system. The substrate temperature was measured by 0.2 mm wire chromel-alumel thermocouple touched to the Mo strip. A spiral-type W wire source was used to evaporate gold. The thickness of the films (60, 85, 100 and 125 nm) and the evaporation rate were controlled. The single crystal Au films were floated from the NaCl crystal in distilled water and supported on a copper microgrids.

Specimens of polycrystalline gold foil, 0.065 mm thick were annealed in vacuum at 980°C for four hours and furnace cooled, prior to electropolishing to produce foils with large electron transparent regions. The foils after this treatment had a [100] preferred orientation. The specimens were thinned in a bath of 200 ml water, 14g potassium cyanide, 6g potassium ferrocyanide, 6g potassium sodium tartrate (solution A), and 0.8 ml ammonia, 4 ml phosphoric acid, and 20 ml H₂O (solution B). The solutions A and B were mixed immediately before use. The samples were also electropolishing in 1 mol-LiCl-methanol at 245 K ($I = 0.25A$, $V = 9.5V$) but the foils had strongly ununiform final thickness. The specimens were washed in water and methanol after electropolishing.

After electropolishing Au foils were PIII implanted to a total dose of $2 \times 10^{17} N^+$ ions/cm². Gold samples were examined in a JEOL 2000FX microscope at an accelerating voltage of 200 kV.

Gold was used in the present study for three reasons: first, the noble character of gold will minimize contamination problems, second, thus far there are no definite evidence about gold nitride formation even when the dose was as high as $2 \times 10^{18} N^+$ /cm², and third, theoretical calculations give for this metal the highest interstitial and substitutional solubility. In the case of low solubility, for instance of helium solubility in nickel the helium tends to precipitate, forming blisters on the surface or gas filled bubbles in the bulk which preferentially nucleate at inhomogeneities like grain boundaries, dislocations or precipitates and cause a significant loss of ductility.

Despite the laboratory experiments of ion implantation using RF [9,14,21] or microwave discharges, little is known of the microstructural effects of these processes. Thus choice of optimum parameters for ion implantation has almost always been made by trial and error.

The present work is an attempt to improve the understanding of the basic processes of structural damage in f.c.c. substance (gold) taking place during PIII.

6. Results

Figures 2 and 3 are micrographs of typical areas, in the single crystal and in the polycrystal foil unimplanted gold specimens. Unfortunately, the all single crystals were damaged during implantation and for further investigations only the polycrystal specimens could be used.

Fig. 3b shows area of a specimen after nitrogen implantation with lots of white circles. There is the possibility that these effects were caused by crystallographic etching or by surface craters produced during implantation [1,24].

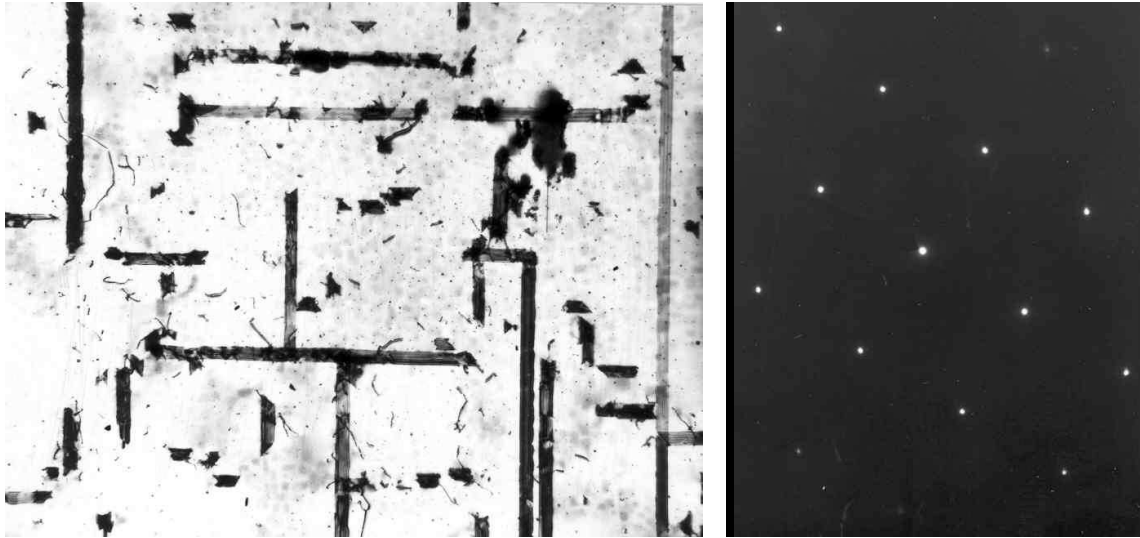


Fig. 2. Micrograph of the single gold crystal. Diffraction pattern with zone axis [100] is inserted

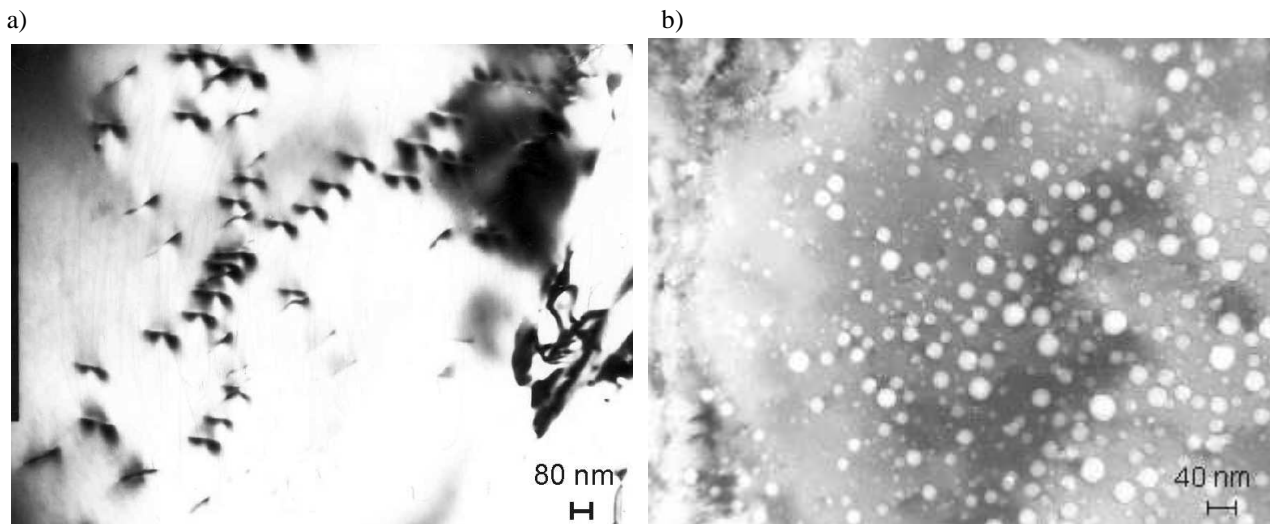


Fig. 3. a) Typical microstructure of polycrystalline unimplanted gold foil, b) micrograph of the implanted polycrystalline gold foil

In this case the contrast of the brighter circles would in general be light, relative to the background and fringes parallel to the edges of the pit or crater would be expected. However, the experimental observations show that the contrast is always bright relative to the background and there are no fringes. Furthermore no trace of these circles has been observed in unimplanted specimens (Fig. 2 and 3a). As the bright circles are found in specimens of gold only if they have been implanted, it is thought that they raised during implantation.

Figure 4 shows the electron micrograph of the typical structure formed by nitrogen ion implantation in a near perforation region of gold foil. The left part of the micrograph, which corresponds to the near-perforation area (the thinnest region of the foil) is without bright circles. In the middle part could be noted increasing amount of small circles. The right part (the thicker region) contains lots of big circles. In other words the bigger the foil thickness the greater bubbles, of course to some extent. The bright circles having obtained a certain limit size stop its growth regardless to the thickness of the foil (Fig. 3b and 4).

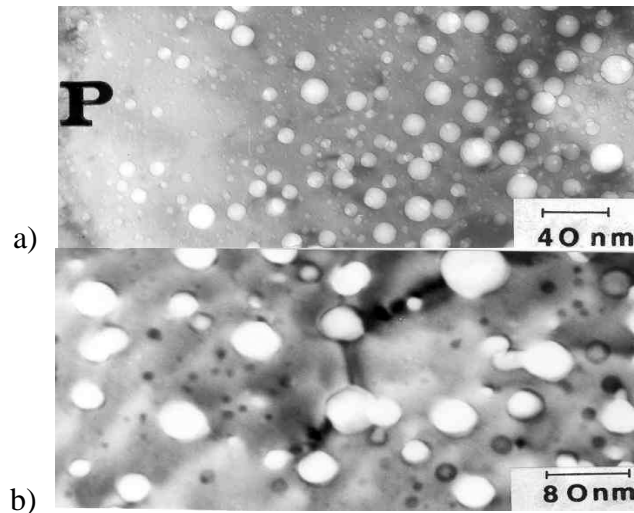


Fig. 4. Micrograph of the structure in a near perforation region of gold foil (perforation is noted P), a) bubbles and dislocation loops in implanted gold foil, b) coalescence of the bubbles

In addition to bright circles there are also observed a background of damage consisting of numerous black dots roughly 8 \AA in diameter and bigger dislocation loops $20\text{-}50 \text{ \AA}$ in diameter (Fig. 4b).

Probable when implanted nitrogen has exceeded their solubility limit in gold begins to precipitate into tiny gas bubbles which coarsen on heating (temperature of foils was 245°C during implantation). This coarsened upon heating and tiny bubbles appeared inside the grains and upon the grain boundaries and dislocation lines (Fig. 3b and 4). These latter bubbles grew larger but became fewer in number upon further heating. The bubbles in the dislocation lines tend to be larger than those in the neighboring area. It can be assumed that the nitrogen might however diffuse along dislocation "pipes", and that this explains the growth of bubbles which have been shown to lie on dislocation lines in Fig. 4b.

Quite frequently bubbles disappeared because they came into contact and coalesced to form a larger bubble; e.g. bubbles in Fig. 4b.

If there would be strain field around the bubble it is insufficient to produce a diffraction contrast effect. It is thought, however, that same strain field does exist, because on several occasions small bubbles have been seen closely associated with larger bubbles; e.g. Fig. 4, where they remained apparently touching without coalescing during heating. Such observation suggest that a short-range repulsion does exist between these bubbles.

Conclusions

It has been observed that pure gold after nitrogen PIII contains a great deal of small gas bubbles. These bubbles can grow as a result of their migration, consequent collision and coalescence.

It may be assumed that bubble creation, migration, coalescence and growth can best be reduced by the introduction of stable precipitates into the metal.

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