First stages of metal surface nanostructuration by He^+ implantation: plasma experiments and molecular dynamics simulations

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Abstract: Interaction of helium ions with metals in particular conditions (high ion fluxes, low kinetic energies, high temperature) is known to lead to the formation of nanostructured porous surfaces. First stages of this process, associated to the formation of vacancy defects in the metal lattice, have been investigated using an ICP-RF plasma source specially designed and equipped with various plasma diagnostics to qualify the implantation conditions. Results of experimental implantations in tungsten are compared to simulated ones obtained by molecular dynamics.

Keywords : Helium ion implantation, ICP-RF plasma source, ion/surface interaction, vacancy defects

1. Introduction

In the course of plasma surface interaction studies for nuclear fusion, it has been unexpectedly found in the mid 2000 that fiber-like nanostructured tungsten (W), so-called "tungsten fuzz," is formed on W surface by helium (He) plasma irradiation [1]. Growth of such structure is of course highly undesired in the frame of fusion, because it induces material embrittlement, which could lead to major degradation of its mechanic properties and release of impurities in the plasma.

From application point of view, nanostructured materials are receiving more and more attention due mainly to their exceptional optical, electrical, magnetic, and mechanical properties. Nanostructured metallic building has potentials to apply in various fields, such as solar absorber [2], catalysis [3], sensors [3], fuel cells [4] etc.

Even if the formation of the nano-patterns has been associated to the growth of He bubbles under the surface, the nano-structuration process has not been entirely understood.

In this double context, we have conducted a study on the first stages of vacancy defect formation in tungsten submitted to helium plasma, since W vacancies, where He accumulates, have been identified to be the sites of He bubble creation. The idea is to investigate the effect of He accumulation inside de W lattice, which requires working at low ion fluxes (to control very low implanted doses) and kinetic energies below the displacement threshold of a W atom by a He ion, to avoid defect formation by direct impact.

In that aim, an ICP-RF plasma source has been designed and implemented in order to precisely characterize the implantation conditions. After implantation, polycrystalline W has been analyzed by nuclear reaction analysis (NRA) to quantify the implanted dose and by positron annihilation spectroscopy (PAS) to evidence the W vacancy defects. Simulation of the He/W interaction has been carried out by molecular dynamics (MD) in conditions as close as possible to the experimental ones.

2. Experiment and similation details

ICP-RF plasma source and samples analyses

An ICP-RF plasma source has been specifically developed at the GREMI to perform implantations in the required conditions: low ions fluxes ($10^{15\text{-}18}$ ions.m^{-2}s^{-1}), low kinetic energies (20 to 500 eV). This requires to handle with a very low electron density plasma, which is not easy to characterize. In our experimental set up implantations take place in a diffusion chamber, connected to the plasma source, and the ion energy is mainly determined by the potential difference between the plasma and the biased substrate. The implantation conditions have been precisely characterized by means of complementary techniques [5]. A Langmuir probe is used to determine the electron density, the plasma and floating potentials etc., a homemade retarding field analyzer was built to evaluate the ion energy flux distribution, and an energy flux diagnostic developed at the laboratory was employed to measure the global energy transferred to the surface during implantations.

The implantation conditions being totally evidenced and controlled, irradiation of annealed-polished W polycrystalline samples have been performed at various ion fluxes, incident fluences, kinetic energies and surface temperatures (173K-873K). Since detection of He in materials by NRA analysis is based on the ^{3}He(d,^{1}H)α nuclear reaction, for implantation the plasma is created in ^{3}He gas.

Implanted He quantity is thus measured by NRA using a 900 keV deuterium beam and collecting the emitted protons. In order to qualify the vacancy defects present before and

formed after the implantation process, the positron annihilation spectroscopy was used. This technique is based on the analysis of the Doppler broadening of the gamma ray signal emitted at 511 keV during the positron annihilation process (DB-PAS) [6].

MD simulation model

To investigate the phenomena occurring during the implantation of helium into tungsten, molecular dynamic simulations are carried out using LAMMPS open source software. A (100) body-centered cubic tungsten crystal box consisting of 17 × 17 × 204 unit cells is built. Periodic boundaries conditions are set in the x [100] and y [010] directions, and free motion is allowed along z [001] to figure the surface of a single crystal. The bottom of the box is composed of a fixed layer of 6 unit cells (20.5 Å) which mimics the unperturbed bulk. The initial velocities of the remaining W atoms are randomly selected from a Maxwell-Boltzmann distribution at desired temperature, which is maintained thanks to a Berendsen thermostat. Substrate thickness is chosen in order to limit to 0.5% the implanted He atom fraction crossing the substrate through the fixed W atoms layer.

Helium ions are treated as atoms, as they are neutralized at the tungsten surface, so classical MD simulations are applicable. He atoms are injected one by one and in a direction normal to the surface. They carry a fixed kinetic energy corresponding to the mean value expected in the experiments.

Handling molecular dynamics only requires the knowledge of inter-atomic potentials and a set of initial conditions. We use the Juslin and Wirth potentials [7]: W-W interactions are described by a modified Ackland-Therford potential and W-He interactions are modelled from DFT study. Finally, He-He interactions in the substrate are described by Beck's potential, which allows He cluster growth. Implantation conditions were chosen to match at the best with experiments.

3. Main results

Plasma analysis: implantation conditions

First of all, to precisely specify the implantation conditions the He plasma was analyzed in different working conditions (He pressure, RF power, distance). Various operating modes of the discharge initiated inside the plasma source have been evidenced, leading to a wide range of ion flux values at the substrate location (see figure 1).

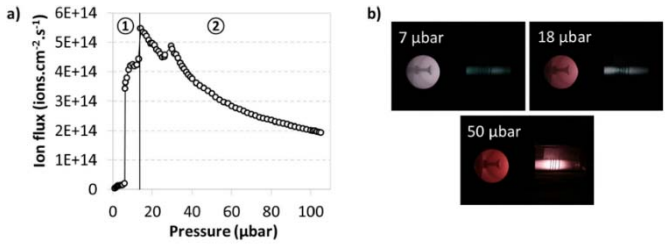

Fig 1. Ion flux measured on the substrate holder biased at -300 V in helium plasma, 35 cm away from the antenna and for an input RF power of 50 W. Two operating regions are evidenced; (b) appearance of the discharge for three pressures belonging to the regions defined in Fig. 3a: 7µbar region 1 just after the sharp increase of the ion flux, 18µbar and 50µbar region 2. On the pictures, the substrate holder inside the diffusion chamber is visible through a circular window at left, and the plasma source (glass tube surrounded by the copper coil antenna) at right.

They have been interpreted in terms of well-known α-γ-capacitely coupled (CC) or inductively coupled (IC) regimes of RF discharges [8,9]. In order to achieve the lowest values of the ion fluxes required for the present work, the discharge has to operate in the CC mode. From homemade retarding field analyzer measurements presented in figure 2, it is seen that in this mode, the ion distribution function could be quite broad. This is a well-known phenomenon in CC-RF plasmas; especially in helium, due to the very simple design of our source (absence of screen). However, thanks to the coupling of the implemented plasma diagnostics, we are able to control the plasma features and managed to find out working parameters leading to reproducible and well-controlled implantation conditions. Moreover, from comparing energy flux measurements with estimation of the deposited energy by the He ions (ion current × maximum energy gained in the sheath) we have also shown that, in most investigated cases, ions can be considered as monoenergetic.

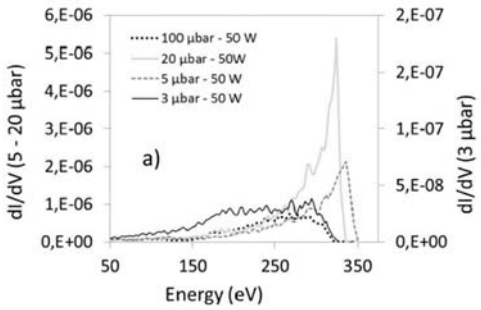

Fig.2. Ion energy distribution function measured with the home-made simplified retarding field analyzer for -300 V substrate bias voltages in helium plasma at various pressures and 50 W

Implantation results

Results of experiments and simulations have shown good agreement, evidencing a saturation step of the implanted He dose inside the W. The defects created before the saturation step are mainly W mono-vacancies filled with He, whereas, larger voids are detected for higher implanted doses [10].

Helium is very mobile in insertion in the W lattice and diffuses easily until it collides with another He atom and forms a dimer. He clusters grow in size and become efficient trapping sites for further incoming He atoms. Thus He accumulates below the surface, causing W lattice distortion as illustrated on figure 3 for a dimer.

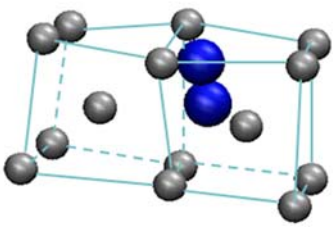

Fig. 3. Result of MD simulation: W (grey spheres) lattice distortion when an interstitial He (blue spheres) dimer is formed.

When a He cluster contains more than 6 atoms, it cannot diffuse anymore and stays at rest. When this occurs a trapping zone is formed locally under the surface where He concentrates, and where bubbles are formed. The pressure is so high in large He clusters that a W atom is able to escape from its crystallographic site to become an interstitial, this is the so called self-trapping process, which leads to the formation of mono-vacancies. When He accumulates in these preliminary vacancies, larger He/vacancy complexes can be created by "trap-mutation" (see figure 4), and finally He bubbles are created.

Thus MD simulations and PAS analysis have evidenced that W vacancies can be formed by the accumulation of He inside the lattice even at He^+ ion kinetic energies lower than the W displacement threshold.

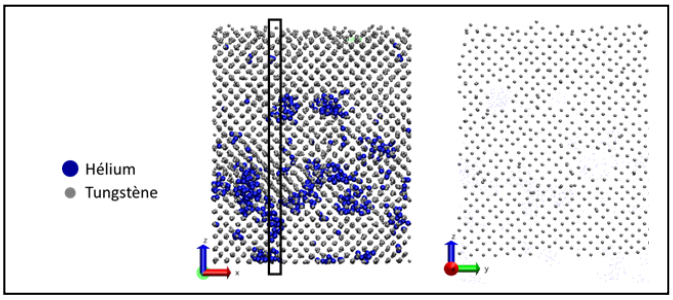

Fig. 4. Result of MD simulation. Left: accumulation of He below the surface and formation of clusters, right: another view of the W lattice (He atoms are removed) showing W vacancies formed at the location of He clusters

When this accumulation takes place close to the surface; results indicate that rupture of the W lattice can occur. This is promoted at low kinetic energies when He is concentrated at the extreme surface and on a very narrow thickness. At 100 eV for instance, emptying of bubbles has been shown, leading to local release of He. When the kinetic energy increases, helium is able to diffuse deeper and is spread over a wider depth and thus the rupture phenomenon occurs for larger implanted doses see figure 5.

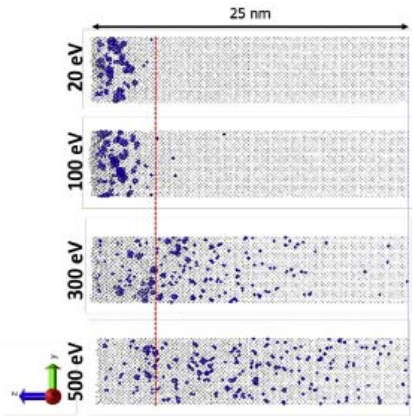

Fig. 5: Results of MD simulation of He implantation in tungsten at room temperature depending on the kinetic energy of the incident helium ions for 1.3×10^{19} $He.m^{-2}$ retention. Snapshots of the implantation simulations. The surface of the W is located at the left side of the images. The gray dots stand for the W atoms and the blue ones for the He atoms.

The effect of the W lattice temperature on this rupture phenomenon has also been studied. It was found to play a less important role than that of the kinetic energy. However, increasing the surface temperature tends to further the W interstitial atoms diffusion and their recombination with vacancies.

In literature fuzz, nano-pillars, porous surfaces etc. formation has been proved to be due to He bubbles/W rupture and to the migration of metal interstitial atoms. The present study allows to get interesting insight into the mechanisms involved at the atomic level in the formation of He bubbles, causing W rupture and in the mobility of W atoms. It clearly highlights that a way to promote the formation of nanostructures will be to work at low kinetic energies, high ion fluxes (to further the accumulation rate) and high surface temperature which promotes bubbles coalescence and ensures high W interstitial atom mobility.

Acknowledgment

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4. References

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