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# Phase formation after nitrogen implantation into molybdenum

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**Abstract**

High fluence nitrogen ion implantation into molybdenum is compared for low energies of 30 keV and below and high energies of 1 MeV at a total fluence between 0.5 and $2.7 \times 10^{18}$ at./cm$^2$. For the low energy implantation, a transformation from cubic $Mo_2N$ towards tetragonal $Mo_2N$ is observed around 580 °C with ex situ X-ray diffraction (XRD), whereas high energy implantation leads to the simultaneous formation of tetragonal $Mo_2N$ and hexagonal MoN in the same temperature range, as observed with in situ XRD. Additionally, ion beam analysis was employed to measure the local atomic concentrations, which can be used for determining the phase formation threshold and the diffusion constant.


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## 1. Introduction

Ion implantation is a widely used process in the semiconductor industry. Modification of metals by ion implantation is a viable method for improved tribological and mechanical surface properties, especially for forming carbides and nitrides, albeit sparsely employed due to process and cost limitation. Nevertheless, there are still open questions on fundamental processes during phase formation under high fluence ion implantation.

Interstitial transition metal compounds are a very interesting class of materials due to the highly localised d-electrons of the metal and the insertion of small atoms – either B, C, N or O – on interstitial sites without ionic or homopolar bonding thus maintaining the metallic properties [1]. The large solubility field allows a sophisticated phase evolution without major structure changes, apart from those in lattice dimensions. Famous examples are the Fe–N system starting from the ε-hcp structure

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[2] and the Ti–O system with the transition from hcp-Ti via cubic TiO and the Magnéli phases $Ti_nO_{2n-1}$ toward rutile $TiO_2$ [3,4].

Ion implantation has been used to investigate the phase formation in these systems, especially for transition metal oxides [5–8] mostly at intermediate energies. In this presentation, the phase formation in the Mo–N system is compared for high fluence high energy implantation at 1.0 MeV and low energy implantation in the range from 5 to 30 keV. Using in situ (XRD), besides ex situ XRD and ion beam analysis after the end of the implantation, during the high energy implantation allows a direct view on the formation kinetics.

## 2. Experiment

Pure molybdenum (99.5%) polished to a mirror-like finish was used as samples. The high energy implantations were performed in an in situ XRD chamber connected to a Tandetron accelerator beamline [9] at 1.0 MeV and a beam current of $\sim$1 μA up to a nitrogen fluence of $1.4 \times 10^{18}$ at./cm$^2$. Additional heating was employed to maintain a sample temperature of 450 or 550 °C. The total implantation time was between 14 and 21 h.

A high vacuum system at a base pressure of $2 \times 10^{-4}$ Pa and a working pressure of 0.2 Pa was used for the low energy implantations with nitrogen plasma immersion ion implantation (PIII). Using a 40.68 MHz r.f. a nitrogen plasma with a composition of approximately 95% $N_2^+$ and 5% $N^+$ is obtained. High voltage pulses between $-5$ and $-30$ kV were applied at a constant repetition rate until the process temperature between 330 and 700 °C was reached. An additional heating system consisting of IR lamps had to be used to achieve sample temperatures of 600 °C and beyond. After the process temperature was reached, the pulse frequency was lowered, thus reducing the average current density, to maintain the temperature. The incident ion fluence was up to $2.7 \times 10^{18}$ nitrogen at./cm$^2$ for treatments between 30 and 75 min. Different ion energies, fluencies and process temperatures were used to ascertain any difference caused by thermal diffusion, ion flux rate and damage production.

The phase composition was studied by X-ray diffraction in Bragg–Brentano geometry with Cu-Kα radiation. A position sensitive detector allowed a scan-time of less than 4 min for a complete XRD spectrum for the in situ measurements in the range $2\theta = 10°$–$80°$ with a stepwidth of 0.02°. The ex situ measurements were performed using a standard instruments with longer scan times. The elemental concentration distributions were obtained from Rutherford backscattering spectroscopy (RBS) using $He^{2+}$ ions with an energy of 2.0 MeV and elastic recoil detection analysis (ERDA) with 200 MeV $^{197}Au^{15+}$ ions at 19° incident angle and a detector placed at a scattering angle of 37°. The data evaluation was performed using RUMP [10] and KONZERD [11] for RBS and ERDA, respectively.

## 3. Results and discussion

The RBS spectra for two samples implanted with 1 MeV nitrogen ions at 450 and 550 °C are shown in Fig. 1, together with a simulated spectrum for pure Mo. Using RUMP, the nitrogen depth profiles shown in the inset can be extracted. The maximum concentration is found near a depth of 600 nm, the value calculated with TRIM [12], albeit the width of the profiles is much larger than the 150 nm straggling. The total retained dose, according to the profiles is 5–7 $\times 10^{17}$ at./cm$^2$.

However, extreme care must be taken in interpreting these data due to the large depth of the implanted nitrogen and the large mass mismatch between the host and the inserted atoms. The cut-off of the profiles at 1.1 μm is caused by multiple collisions inside the target which are not included in the RUMP simulation. A certain influence of those at lower depths must be present, which is hard to quantify. Nevertheless, the real data should contain a more pronounced and deeper reaching tail towards the right as well as a small shift of the maximum concentration towards larger depths.

Additionally, the absolute concentration may be smaller than the calculated values. During the implantation, competing processes of nitrogen insertion and diffusion broadening are occurring