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Thermal and chemical stability of the β-W_2N nitride phase

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ABSTRACT

Pure Be, W and Be:W mixed coatings with nominal compositions of (5:5) and (1:9) were deposited on silicon plates and implanted at room temperature with 30 keV N^+ ions with fluences up to 5e17 ions/cm^2. Ion beam and X-ray diffraction analysis evidenced the formation of the α-Be_3N_2 and β-W_2N nitrides. The identified tungsten nitride phase evolves from a BCC W lattice to a BCC W(N) solid solution after irradiating at a fluence of 1e17 N^+/cm^2 and to the compact FCC β-W_2N structure at 5e17 N^+/cm^2. Thermal stability of β-W_2N was investigated by annealing the coatings for 1 h up to 1073 K. The results point to the release of non-bonded nitrogen solute in β-W_2N over the annealing range and to the thermal stability of the nitride phase up to 1073 K.

1. Introduction

The International Thermonuclear Experimental Reactor (ITER) will use beryllium (Be) and tungsten (W) as plasma facing materials (PFM) in the first wall and divertor, respectively. Be particles eroded from the first wall will be mainly guided by the magnetic field towards the divertor and the composition of this area will evolve significantly over time during the reactor operation, leading to the formation of Be-W mixed layers with different stoichiometries [1]. Another source of co-deposits could be the injection of seeding gases as nitrogen (N) to reduce the power heat loads in the divertor target, while a significant part of the seeding impurities will be accelerated and co-deposited with the Be-W layers [2]. Due to the affinity of N to react with Be and W, the use of N as seeding gas will result in the formation of nitrides [2–5] and it is important to identify the composition and thermal stability of the new phases in order to predict the behaviour of PFM over time under irradiation and annealing. WN_x protective films are commonly used in other research domains due to their extreme hardness, high electrical conductivity or high chemical stability [6,7], and the particular formation of tungsten nitrides may result in a decrease of the erosion rates, enhancing the lifetime of the exposed surfaces [6]. Previous experiments revealed that the irradiation of pure Be and W films at low temperature with high fluences of N ions lead to fast saturation of the exposed surfaces such that the thickness of the enriched layers is comparable to the in-depth range of the impinging ions [3,5]. Experiments performed at elevated irradiation energies are important for the research community since abnormal plasma instabilities will easily accelerate particles [8,9] and runaway electrons towards the divertor region. The implantation of N ions on pure Be with incident energies up to 2.5 keV per atom resulted in the formation of a saturated and thermally stable α-Be_3N_2 superficial layer up to a temperature of 1000 K [3]. For the case of pure W coatings, the irradiation with N ions with energies up to 5 keV per atom evolved to a saturated WN layer, which became unstable under annealing at temperatures higher than 600 K [5]. The results agree with the available thermodynamic data. Two beryllium nitride phases with similar standard enthalpies of formation ($\Delta H_{f,298}$) are identified in the binary Be-N diagram [4]: cubic α-Be_3N_2 remains stable from room temperature up to about 1700 or 1800 K ($\Delta H_{f,298} = -590$ kJ/mol) and hexagonal β-Be_3N_2 is typically formed at normal pressure and higher temperatures ($\Delta H_{f,298} = -572$ kJ/mol) [3,10]. Two tungsten nitride phases are also present in the predicted N-W binary system [5]: hexagonal WN, from room temperature up to about 600 K ($\Delta H_{f,298} = -24$ kJ/mol), and cubic β-W_2N, which typically grows at higher temperatures ($\Delta H_{f,298} = -72$ kJ/mol) [11]. The thermal stability of the β-W_2N phase remains an open question although it is thought that a new phase transition should only occur at extremely high temperatures, possibly higher than 2000 K [5,11]. Other open question is the possibility to have preferential growth of beryllium nitrides rather than those of tungsten, since they present much lower heats of formation (ΔH_f). A third parameter

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that may modify the final composition of the nitrides is the energy of the N impinging ions, since higher incident energies lead to deeper ranges of N ions within the targets and possibly, to an increment in the final W/N elemental ratios, retarding the saturation threshold for N [12]. The reaction kinetics involving energetic ions is also favourable to the formation of compounds at temperatures lower than those ones predicted by the available phase diagrams and, moreover, it was already identified the simultaneous growth of both WN and W_2N nitride phases in PFM [13]. The aim of the present experiment was to investigate the growth and thermal stability of nitride phases in mixed Be-W layers by implanting N ions at elevated incident energies. In particular, it should be interesting to observe the formation of tungsten nitrides in presence of a significant Be content.

2. Experiment and methods

Pure Be, W and mixed Be:W coatings with stoichiometric ratios of (5:5) and (1:9) were deposited by the thermionic vacuum arc method (TVA) [14,15] on mirror quality silicon (Si) plates with nominal thicknesses of 300 and 400 nm. With the purpose to investigate the reactivity of the Be:W films with nitrogen, in a first campaign the coatings were irradiated with 30 keV N^+ ions at room temperature. This energy is typical used in ion beam laboratories and it was chosen for the present experiments. The irradiation was performed with nominal fluences of 1e17 and 5e17 ions/cm^2 and current densities of 3.2 µA/cm^2. At this incident energy, the calculated in-depth (Rp) and straggling ranges (ΔRp) of N^+ ions inside the films are about 85 nm and 21 nm for pure Be and of 29 nm and 16 nm for pure W, respectively, assuring that the implantation depth range remains inside the Be:W layers [12]. From the first irradiation campaign the formation of the β-W_2N phase was identified in all the films containing W, which motivated us for a second set of experiments with the purpose of evaluating the thermal stability of the nitride phase. At this time, Be:W (5:5), Be:W (1:9) and pure W coatings were implanted once again with 30 keV N^+ ions at room temperature with a fluence of 5e17 ions/cm^2 and a current density of 5.0 µA/cm^2, and annealed afterwards in vacuum in the temperature range 573 K–1073 K with steps of 100 K over 1 h and a base pressure close to 1e−7 mbar. Before and after the implantation campaigns, the thickness of the coatings and the elemental depth profiles of both W and Si were quantified by Rutherford backscattering spectrometry (RBS) using 2.0 or 2.2 MeV $^4He^+$ incident beams. Additionally, the Be, N and O depth profiles were evaluated by Elastic backscattering spectroscopy (EBS) making use of incident H^+ ion beams at lower energies, 1.0–1.6 MeV, in order to enhance the backscattering yield of light elements [16,17]. Moreover, and for the analysis of the present samples at these precise energies, the N profiles are not hindered by their superposition with the yields of Si. The EBS analysis is particularly useful to evaluate any release mechanism of N induced during the annealing route. Finally, the formation of the nitride phases was identified by X-ray diffraction (XRD) performed in a grazing geometry in order to enhance the pattern yields arising from the thin coatings and mitigate the influence of the substrates. The method is particularly useful for the present investigation, since the unit cells of light compounds as beryllium nitrides induce predominant incoherent scattering, leading to weaker diffraction patterns [18]. The sensitivity of the analysis is really enhanced in thicker coatings. Nevertheless, the depth ranges of 30 keV N^+ ions inside the present coatings are appropriate for the identification of heavier tungsten nitride phases [12,18]. The experiments were carried out with a Bruker-AXS D8 Discover diffractometer by using Cu-K$_{\alpha 1}$ incident X-ray beams at a glancing angle of 1.5° and 2θ angular scans in the range from 15 to 75°. The diffraction patterns were identified by the ICDD data library [19].

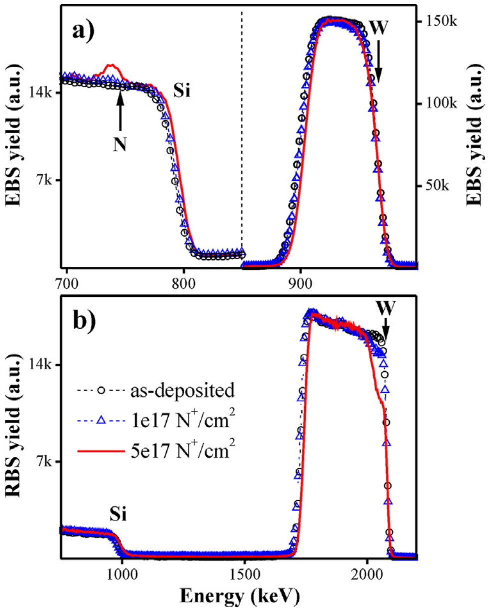

Fig. 1. EBS (a) and RBS (b) spectra collected from Be:W (1:9) before and after N^+ irradiation.

3. Results and discussion

3.1. Nitride formation at room temperature

As an example of the analytical procedure, Fig. 1a presents EBS spectra collected from a Be:W (1:9) coating before and after implantation by using a 1.0 MeV H^+ ion beam. The isolated W backscattering yield is identified at higher energies and the inelastic scattering of incident protons by ^9Be and ^{14}N becomes visible and superimposed with the backscattering yield of Si from the substrate. The energies corresponding to the presence of N and W in the surface layers are indicated by vertical arrows. The elemental depth quantification in the irradiated samples points to higher retention rates of N in pure Be coatings. As example of the quantitative results, N contents of 1.00e17 at/cm^2 and of 4.80e17 at/cm^2 were evaluated from the Be coatings after irradiation with fluences of 1e17 N^+/cm^2 and 5e17 N^+/cm^2, respectively (see Table 1), leading to corresponding retention rates of 1.00 and 0.95. For the other target compositions the final N content significantly decreases by increasing the W amounts. The RBS spectra obtained from the Be:W (1:9) coatings by using 2.0 MeV ion beams are presented in Fig. 1b. A smooth fluctuation can be seen in the W profile arising from the TVA deposition procedure. Nevertheless, the W depth profile is quite uniform and after N irradiation, it deeply decreases at the surface layers due to the addition of N, and it is possible to evaluate the depth of the implantation zone using this variation. Apart from the Be coatings, we also notice that the thickness of the remaining targets are not significantly affected by erosion, typically due to the scattering caused by heavy W at the surface. The same mechanism may explain the lower N contents in these samples. Table 1 summarises the quantitative results of the analysis. Estimated errors of 5% are assumed due to uncertainties in the stopping power cross sections of ions in matter [12].

Fig. 2a presents the diffractograms obtained from Be coatings, before and after 30 keV N^+ implantation with nominal fluences of 1e17 and 5e17 N^+/cm^2. The sensitivity to detect light elements and compounds in thin films by grazing XRD is very low [18]. Nevertheless, the characteristic peak lines for Be become visible at 45.8°, 50.9°, 52.8° and also at 70.8° (not presented in Fig. 2a), corresponding to the diffraction pattern for the planes (100), (002),

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