57Fe Mössbauer study of epitaxial TiN thin film grown on MgO(100) by magnetron sputtering

Qi, B.; Gunnlaugsson, H.P.; Mokhles Gerami, A.; Gislason, H.P.; Ölafsson, S.; Magnus, F.; Mølholt, Torben Esmann; Masenda, H.; Tarazaga Martín-Lueugo, A.; Bonanni, A.

Total number of authors:
18

Published in:
Applied Surface Science

Link to article, DOI:
10.1016/j.apsusc.2018.09.107

Publication date:
2019

Document Version
Peer reviewed version

Link back to DTU Orbit

Citation (APA):
57Fe Mössbauer study of epitaxial TiN thin film grown on MgO(100) by magnetron sputtering


PII: S0169-4332(18)32523-6
DOI: https://doi.org/10.1016/j.apsusc.2018.09.107
Reference: APSUSC 40411

To appear in: Applied Surface Science

Received Date: 26 April 2018
Revised Date: 18 August 2018
Accepted Date: 12 September 2018


This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.
$^{57}$Fe Mössbauer study of epitaxial TiN thin film grown on MgO(100) by magnetron sputtering


Abstract

The properties and performance of TiN thin films are closely related to the concentration and mobility of lattice defects in the thin film structures of TiN. This makes a local atomic scale study of TiN thin films an ever-growing demand. Emission $^{57}$Fe Mössbauer spectroscopy (eMS) is a powerful tool in this regard, which we apply here to study an ultrathin TiN film epitaxially grown on MgO (100). With the help of theoretical calculations, our results show that most implanted Fe ions adopt a $2^+$ valence state and locate at the Ti sublattice in the bulk-like single crystalline grains, with the rest Fe residing at the grain boundaries as interstitials. A small percentage of nitrogen point defects (vacancy $V_N$ and interstitial $N_I$) are observed in the bulk-like crystalline grains. A temperature-dependent, interstitial $N_I$ mediated site-exchange between $N_I$ and $V_N$ inside the crystal grain are deduced via a $N_2$ dimer like diffusion of $N_I$ through the crystal grains in the temperature range of 540 - 620 K. This is interesting in the perspective of exploring the catalytic property of TiN nanostructures. The titanium vacancy ($V_{Ti}$) is only detected at the grain boundaries. Annealing up to 813 K, both the $V_N$ and $N_I$ are annihilated in the crystalline grains and the $V_{Ti}$ is fully recovered with healing of the grain boundaries. However, no evidence of ferromagnetism due to dilute implantation of $^{57}$Mn/$^{57}$Fe and or structural defects in the film is obtained.
This suggests that the so far reported dilute magnetism and defect-induced ferromagnetism in TiN nanostructures requires a further systematic investigation.

Key words: TiN, Mössbauer spectroscopy, epitaxial thin film, defects

1. Introduction

As a prototype transition-metal nitride (TMN), TiN is an important material in hard coatings and modern microelectronics [1] [2]. It possesses excellent hardness, chemical stability, high melting temperature, appealing tuneable optical and electrical properties, such as the unique metallic behaviour in the visible and near-IR ranges [3] as well a disorder-induced metal-insulator transition properties [4]. TiN thin films have been widely used as wear- and corrosion-resistant coatings, diffusion barriers, gate electrodes in field-effect transistors (FET), as replacement of polycrystalline Si in large-scale integrated circuits, contact layers in solar cells, metal-insulator-superconductor (MIS) tunnel junctions [5] [6] [7] and low-loss plasmonic materials [8]. Furthermore, TiN is known to have a low electromagnetic loss at microwave frequencies and has found applications in low-loss superconducting qubits, microwave resonators for qubits and microwave kinetic inductance detectors [9] [10]. Recently, anomalous defect-induced magnetic and electromagnetic properties have been reported for both as-prepared and Fe-doped TiN nanocrystals [10] [11], although bulk TiN is non-magnetic. This renders TiN an appealing material for multi-functional ferromagnetic materials in spintronic applications.

TiN thin films can be synthesized by various deposition methods. Magnetron sputtering has proved to be a successful technique promoted to an industrial scale for many years [12], including the growth of advanced functional thin films used for solar cells in recent years [13] [14]. TiN stabilizes in the face centred cubic (FCC) structure. However, non-stoichiometry and possible structural defects commonly exist in TiN thin films grown by magnetron sputtering. The stoichiometry and microstructure defects in TiN have profound effects on the above-mentioned mechanical, electrical, optical, local magnetic and electromagnetic properties [15] [16] [17]. Especially with the ever-growing interest in the application of nanoscale materials in various quantum device architectures, atomic scale characterization of the material composition and microstructure defects is highly desirable in order to tune the material properties for the appropriate applications. Mössbauer spectroscopy is particularly useful in this regard, due to its sensitivity to the immediate atomic environment of the probe nucleus through electric interaction and magnetic hyperfine interaction (up to second next nearest neighbours) [18]. Using implantation of
radioactive parent isotopes (emission Mössbauer spectroscopy, eMS) in the sample of interest, one can study extremely dilute levels (~10^-3 at%) [19]. With eMS, the dilute Fe atoms in ZnO/AlN/GaN were confirmed in a paramagnetic state, ruling out the assumption of ordered magnetic origin of the dilute magnetic properties in ZnO/AlN/GaN [20] [21] [22].

Conventional $^{57}$Fe Mössbauer spectroscopy was used to test the assumption about the occupation of excess nitrogen in the tetrahedral voids of TiN (B1) structures and annealing-assisted diffusion contribution to the intrinsic stress of the (Ti, Fe)N coating [23]. The spectroscopy was also carried out on Ti films and TiN coatings following a room temperature (RT) implantation of $^{57}$Fe ions with an energy of 70 keV and a dose of 2×10^{16} Fe ions/cm² [24]. The implanted $^{57}$Fe ions were found to individually occupy the local Ti sites forming α-Ti(Fe) and β-Ti(Fe) structures in the Ti foil. In the TiN coating, three components were identified: the first component (~ 33%) was due to the implanted $^{57}$Fe ions replacing the N sites surrounded by Ti neighbors, forming structures like α-Ti(Fe) and β-Ti(Fe); the second, which was the main component, appeared as the Fe ions replacing the Ti atoms in the Fe₂N phase with Fe in regular lattice sites; the third component was in FeN phase, in which the Fe ions were located at highly perturbed sites at the grain boundaries. After annealing at 773 K in air, the Ti(Fe) phase transformed to the intermetallic Ti₂Fe compound. The Fe₂N phase was stable up to 873 K, whereas the FeN formed at the grain boundaries was converted to superparamagnetic a-Fe₂O₃, and gradually into magnetically ordered a-Fe₂O₃ due to oxidation. These early studies demonstrate that the $^{57}$Fe Mössbauer spectroscopy is useful to follow compositional and structural changes of TiN coatings with doping, implantation and annealing of Fe ions. However, concerning the recent demand for atomic scale investigation of possible diluted or defect-induced magnetic properties of TiN nanostructures, a further $^{57}$Fe Mössbauer spectroscopy study on up-to-date TiN structures with Fe doping at truly dilute level (a dose < 2×10^{16} Fe ions/cm²) is needed.

In this work, we employ $^{57}$Fe eMS by implantation of short-lived radioactive $^{57}$Mn⁺ ions in TiN at an extremely dilute level using the ISOLDE facility at CERN [25] [19]. This is especially powerful for atomic scale investigation of local structure defects and the possible diluted magnetic properties of TiN nanostructures. We chose an ultrathin (40 nm) epitaxial TiN film grown on a single crystalline MgO (100) substrate, which is an interesting gate stack system in future non-Si based metal-oxide-semiconductor devices. Furthermore, the epitaxial ultrathin TiN film, with well-defined grain boundaries and single crystalline grains/nanostructures, is ideal for studying annealing-induced structural changes and possible defect-related magnetic properties of the TiN at the atomic scale. The eMS results are then
compared with calculations using density functional theory (DFT) within the Wien2K package [26] for interpretation of spectral components.

2. Material and experimental method

The TiN thin film was grown on a single-crystalline MgO(100) at 400 °C by reactive magnetron sputtering with a Ti target (99.99%) in an argon (Ar, 99.999%) and nitrogen (N₂, 99.999%) gas mixture (20:1) at 0.4 Pa with an applied power of 100 W. The film shows epitaxial single crystalline cubic (fcc) TiN (100) structure as shown by the X-ray diffraction (XRD) in Fig.1 and with a low roughness at a thickness of 40 nm. The lattice parameter is around 4.248 Å, larger than that of a bulk TiN crystal (4.242 Å) due to compressive strain [27].

The ⁵⁷Fe eMS experiments were carried out at the ISOLDE facility at CERN. ⁵⁷Mn⁺ (T₁/₂ = 90 s) beams were produced by 1.4 GeV proton-induced fission in a heated UC₂ target followed by an element-selective laser ionization [28]. With acceleration to 50 keV and magnetic mass separation, a clean beam of ⁵⁷Mn⁺ with the intensity of a few times 10⁸ ⁵⁷Mn⁺/s was obtained. The ⁵⁷Mn⁺ ions were then implanted into the TiN (100) thin film on the MgO (100) substrate at an incident angle θᵢ of 30° relative to the sample surface normal.

⁵⁷Fe eMS spectra were recorded using a single line parallel plate avalanche detector (PPAD) equipped with an ⁵⁷Fe-enriched stainless steel electrode, mounted on a conventional drive system outside the implantation chamber at emission angle θₑ of 60° relative to the sample surface normal and 90° relative to the beam direction. The system was calibrated using implantations into α-Fe foils. The intrinsic line-shape of the detector is best described with a Voigt profile having Gaussian broadening of 0.1 mm/s and Lorentzian broadening of 0.34 mm/s. In the analysis, lines were analysed with additional Gaussian broadening. Isomer-shifts and velocities are given relative to the centrum of the spectrum of a-Fe at RT.
The total implanted local concentration of $^{57}$Mn$^+$ was estimated to be less than $10^{-4}$ at.% based on the maximum implanted fluence ($\sim 2 \times 10^{12}$ $^{57}$Mn$^+$/$\text{cm}^2$). The sample was heated with a halogen lamp from the backside. In some cases, after implanting $^{57}$Mn at the specified temperatures, the sample was swiftly removed from the implantation chamber and quenched in liquid nitrogen at $\sim 110$ K, to study the possible implantation-induced disorder in the sample before being annealed.

3. Computational method

Kohn-Sham equations were solved to calculate the nuclear hyperfine parameters for a series of Fe sites in different local electron environments in the face-centred cubic (fcc) lattice structure of TiN with experimental lattice constant. The general potential linear augmented plane wave (FP-LAPW) method [29] which is based on the density functional theory (DFT) was used to solve the Kohn-Sham equations in Wien2k Code [26]. In the calculations, the generalized gradient approximation (GGA) in the form of Perdew Burke Enzerhof (PBE) [30] was applied for the exchange-correlation potential. The electronic configurations of the elements in TiN are Ti: $[\text{Ar}]3d^24s^2$ and N: $[\text{He}]2s^22p^3$. The electronic configuration of Fe is $[\text{Ar}]3d^64s^2$. In order to create these electronic configurations, a separation energy $-7$ Ry was taken as the boundary between the core electron wave functions and those of the valence electrons. The radii of the muffin tin atomic spheres of Ti, N and Fe were taken to be 2.18, 1.77, and 2.22 a.u., respectively. The atomic radii were chosen such that the mutual overlaps between all kinds of combination of interstitial and atomic spheres are within the permissible limit of the atomic-sphere approximation. The maximum value of the angular momentum quantum number for the wave function expansion inside the Muffin-tin spheres were confined to $l_{\text{max}}=10$. The cut-off parameter, $(R_{\text{MT}}K_{\text{max}})$ was set to 7.0, where $R_{\text{MT}}$ is the smallest of all atomic sphere in the unit cell and $K_{\text{max}}$ is the magnitude of the largest K vector in the plane wave expansion, while the charge densities were expanded as Fourier series up to $G_{\text{max}}=12$ (Ryd)$^{1/2}$. A supercell size of $2 \times 2 \times 2$ and a mesh of $(7 \times 7 \times 7)$ k-points in the irreducible part of the first Brillouin zone were used in the calculation. The self-consistent calculations process was repeated until the total energy converged to 0.0001 electron charge. In this approach, the isomer shift $\delta$ was calculated from the relative contact density $\rho$ between the absorber and source isomers as [31]:

$$\delta = \alpha (\rho_A - \rho_s)$$ (1)
where, $\rho_A$ and $\rho_S$ are the charge densities at the nuclei in the absorber (A) and sample (S) material, respectively, and the body-centred cubic (bcc) lattice structure of Fe was considered as sample (S). $\alpha$ is calibration constant, which was set to $\alpha = -0.29$ a.u.$^3$·mm/s [32].

The quadrupole splitting $\Delta E_Q$ was obtained from the principal component $V_{zz}$ of the electric field gradient. The electric field gradient tensor (EFG), expressed by its principal component $V_{zz}$ and the asymmetry parameter $\eta$, gives the quadrupole splitting as:

$$\Delta E_Q = \frac{eQ_{zz}V_{zz}}{2} \sqrt{1 + \eta^2 / 3}$$  \hspace{1cm} (2)

where $e$ is the elementary charge and $Q = 0.16 \times 10^{-28}$ m$^2$ [33] is the nuclear quadrupole moment of the 14.4 keV Mössbauer state of $^{57}$Fe.

4. Results and discussions

4.1. Experimental and computational results

![Fig.2: (a) $^{57}$Fe eMS spectra of the TiN thin film after implantation of $^{57}$Mn$^+$ and (b) the corresponding area fractions of the components with the implantation temperature from 303 K to 813 K.](image)
Fig. 2(a) shows the selected $^{57}$Fe eMS spectra obtained after implantation of $^{57}$Mn into the TiN thin film in the temperature range of 303 - 813 K. The spectra were analysed using the program Vinda [34] with Voigt line shapes in accordance with the intrinsic line-shape of the detector.

The spectra are dominated by a single line (SL) with $\delta \sim 1$ mm/s, which is the main feature of the spectrum obtained at 813 K. By extrapolating the position of this line at 813 K to RT using the second order Doppler (SOD) shift, it coincides nicely with the dominating single line of the spectrum obtained at RT.

The spectrum broadening within velocity range of $v = -1.0$ to -0.5 mm/s at temperature < 813 K points to the presence of one or more prominent spectral component(s) with $\delta \sim 0.5$-1 mm/s. However, fitting with single lines would lead to unphysical isomer-shifts, so more likely, these features are due to quadrupole split components with the left-hand legs underneath the dominating SL. Therefore, in the final analysis, a minimum of two components (DB1 and DB2) was required to obtain a sufficient description of the experimental data.

In the spectra obtained at 541 K and 616 K, the single-line SL appears broader than at both the lower and higher temperatures. This could be due to temperature dependent broadening of the SL or due to the presence of an additional spectral component. Both hypotheses were tested and adding a new quadrupole split component (DB3) with $\delta$ similar to that of SL was clearly favoured in fitting.

The final analysis was then performed simultaneously with the above mentioned four components, where the resonance position of each line was set to follow the temperature dependent-SOD shift and the Gaussian broadening of each line was assumed to be temperature independent. The fitting parameters at RT (303 K) are listed in Table 1. The relative area fraction of the individual component as a function of temperature is plotted in Fig. 2(b).

**Table 1:** Summary of hyperfine parameters from the data fitting of eMS spectra in Fig. 2(a) and suggested site assignment of the components. $\delta_{\text{RT}}$ and $(\Delta E_Q)_{\text{RT}}$ refer to the isomer shift and the quadrupole splitting at room temperature (RT), respectively, $\sigma$ refers to the additional Gaussian broadening of the spectral lines after subtracting the experimental line width of the detector (0.1 mm/s).

<table>
<thead>
<tr>
<th>Component</th>
<th>$\delta_{\text{RT}}$ (mm/s)</th>
<th>$(\Delta E_Q)_{\text{RT}}$ (mm/s)</th>
<th>$\sigma$ (mm/s)</th>
<th>Suggested site assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>SL</td>
<td>0.79(1)</td>
<td>0</td>
<td>0.073(5)</td>
<td>Substitutional Fe$^{2+}$ on Ti in defect-free TiN cubic</td>
</tr>
<tr>
<td>DB1</td>
<td>0.05(2)</td>
<td>1.93(3)</td>
<td>0.02(1)</td>
<td>Interstitial Fe</td>
</tr>
<tr>
<td>DB2</td>
<td>-0.04(1)</td>
<td>0.57(1)</td>
<td>0.11(1)</td>
<td>Interstitial Fe</td>
</tr>
<tr>
<td>DB3</td>
<td>0.79(4)</td>
<td>0.69(12)</td>
<td>0.07(2)</td>
<td>Substitutional Fe$^{2+}$ on Ti in lattice-defect TiN cubic</td>
</tr>
</tbody>
</table>
As shown in Table 1, the additional Gaussian broadening of the lines ($\sigma$) are all very narrow, much lower than what is expected for amorphous environments ($\sigma \sim 0.3-0.4$ mm/s [35]). This suggests the good crystalline environments of the probe atoms.

As shown in Fig. 2(a) and Table 1, the dominant SL component with $\delta_{RT} \sim 0.8$ mm/s is characteristic of Fe$^{2+}$ on a cubic site. The components DB1 and DB2 are characterized by the low $\delta_{RT}$ values (~0.0 mm/s) and significant ($\Delta E_Q$)$_{RT}$ values (1.93 mm/s and 0.57 mm/s, respectively), which we tentatively assign to interstitial Fe (Fe$_I$) in highly-distorted lattice environment. They count for a minor part of the spectral area (less than 20%) at RT and decrease gradually with temperature. There is no evidence of an Fe$^{3+}$ component, which would have shown a sextet type of spectrum due to slow paramagnetic relaxations.

The doublet DB3 has similar $\delta_{RT}$ and $\sigma$ values as the dominant SL, but with a larger ($\Delta E_Q$)$_{RT}$ value of 0.69 mm/s. This suggests that the DB3 can also be considered as Fe$^{2+}$ occupying a Ti sublattice site, but in a lattice defect environment. Furthermore, as shown in Fig. 2(b), the changes in fractional areas of DB3 and SL with temperature follow an opposite trend. This indicates that there is a temperature-dependent dynamic site-exchange between SL and DB3. We will discuss this point in more detail in the next section.

Fig 3: The $^{57}$Fe eMS spectra measured (a) on-line during implantation and (b) off-line during quenching in the liquid nitrogen (110 K) after implantation of $^{57}$Mn into the TiN thin film, and (c) the corresponding area factions of the components at the indicate.
Figs. 3(a) and (b) show the $^{57}$Fe eMS results obtained during on-line implantation at 303 K, 357 K and 450 K, and the spectra measured off-line upon rapid cooling in liquid nitrogen to ~110 K during the decay of $^{57}$Mn after implantation at the temperatures specified above. The changes in the area fractions of the corresponding components are plotted with their error analyses in Fig. 3(c). Except a notable reduction in the area fraction of the main component SL in the offline spectra due to the natural decay of the implanted $^{57}$Mn isotope, there is no significant difference between the off-line and the on-line spectra. This confirms that the minor components are related to the intrinsic structural defects in the sample, indicating that the local lattice structure of TiN is preserved at the implantation temperature; the interstitials and vacancy defect sites have lower Debye temperatures than the dominant substitutional site.

The hyperfine parameters for different configurations of Fe on substitutional and interstitial sites in TiN were simulated, the results are summarized in Table 1s in Supplementary Material. As shown in Table 1s, although some of the calculated substitutional configurations can explain the SL and DB3 components, they cannot explain the components with isomer shift ~0.0 mm/s (DB1 and DB2). Because of the recoil imparted on the daughter $^{57}$Fe atom in the $\beta^-$ decay of $^{57}$Mn or implantation directly on interstitial sites, looking for interstitial defects seems plausible. Therefore, the configurations with Fe atom as interstitials located at the centre of the cubic TiN lattice with and without $V_{Ti}$ or $V_N$ are also calculated and included in Table 1s. Comparison of the computational results and the eMS measurement results are shown in Table 2.

Table 2: Comparison between theoretical and experimental measured hyperfine parameters for substitutional (Fe$_s$) and interstitial (Fe$_I$) configurations ($x$ denotes not detected).

<table>
<thead>
<tr>
<th>Calculated</th>
<th>Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>$\delta$ (mm/s)</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1</td>
<td>0.84</td>
</tr>
<tr>
<td>2</td>
<td>0.76</td>
</tr>
<tr>
<td>3</td>
<td>0.69</td>
</tr>
<tr>
<td>4</td>
<td>0.65</td>
</tr>
<tr>
<td>5</td>
<td>0.74</td>
</tr>
<tr>
<td>6</td>
<td>0.53</td>
</tr>
<tr>
<td>7</td>
<td>0.82</td>
</tr>
<tr>
<td>8</td>
<td>0.71</td>
</tr>
<tr>
<td>9</td>
<td>0.79</td>
</tr>
</tbody>
</table>
Table 2 shows that the Fe$_5$-defect-free cubic configuration (#1 in Table 2), which has $\delta = 0.84$ mm/s and $\Delta E_Q = 0$ mm/s, agrees well with the experimental values of the singlet line component SL, which has $\delta = 0.80$ mm/s and $\Delta E_Q = 0.0$ mm/s, respectively. The configuration Fe$_5$ with two nitrogen vacancies at the angles of $180^\circ$ (Fe$_5$-2V$_N$ ($180^\circ$), #7 in Table 2), which has calculated values of $\delta = 0.82$ mm/s and $\Delta E_Q = 0.69$ mm/s, is very close to the DB3 component which has been measured with $\delta = 0.79$ mm/s and $\Delta E_Q = 0.69$ mm/s, respectively.

4.2. Discussion

The single line (SL) fits reasonably well with the calculated results for Fe$_5$ (#1 in Table 2). However, the calculated values for some of the vacancy type defects (#2-5 & #8-9 in Table 2) indicate that such defects might also contribute to the SL and could explain the slight broadening of the line. Only the Fe$_5$-2V$_N$ ($180^\circ$) (#7 in Table 2) gives rise to significant quadrupole splitting to explain the large $\Delta E_Q$ value of DB3 component.

The only defects found with isomer-shifts $\approx 0$ mm/s, are interstitial type of defects. Isolated interstitial atoms (#10 in Table 2) would give rise to a line without quadrupole splitting. Although such component could be buried within the DB2 component, in most cases, some sort of interstitial-vacancy defect complex is needed in order to account for the noticeable $\Delta E_Q$ values of DB1 and DB2. Furthermore, the calculated $\Delta E_Q = 1.10$ mm/s and 1.34 mm/s are not consistent with the measured $\Delta E_Q = 1.93$ mm/s and 0.57 mm/s values of component DB1 and DB2. To solve this discrepancy, the particulate sceneries considered in the theoretical calculations and the sample conditions needed to be revisited.

Considering the thin film growth conditions, grain boundaries are commonly observed in thin films grown by magnetron sputtering on heterogeneous substrates [36]. Although our TiN thin film was
epitaxially grown on MgO (100), the growth did not follow an ideal layer-by-layer mode. With an established epitaxial relationship with MgO (100) substrate starting from growth temperature at 200 °C, the film grown at 400 °C is the result of purely geometrical development from growth at 200 °C, where the film is dominated with small flat rounded [200]-oriented grains about 14.8 nm wide and some (111)-faceted pyramidal grains scattered on the surface nm [27]. This means that on average there is a grain boundary in every 14.8 nm distance along the surface, which counts the grain density around 7% per nm. With growth temperature increasing to 400 °C, the faceted pyramidal grains rapidly give way to the dominant fast growth of large flat rounded grains, which reach a width of approximately 57.3 nm. Thus, on average, there is a grain boundary every 57.3 nm along the surface, i.e. with a grain boundary density of around 2% per nm. The grain boundaries are frequently seen on the TiN thin film as highlighted by the dark-lines added around the grains in the SEM images in Fig.4.

Based on the results in Table 2 and the TiN thin film growth conditions, we discuss the results in more details in the following subsections.

### 4.2.1. Site assignments for components SL and DB3

As illustrated in Fig.5(a), the implanted Fe atom occupies a Ti lattice site in a regular octahedral unit cell surrounded by six nearest N neighbour atoms (1, 2, 3, 4, 5 and 6). This gives a homogenous electron density distribution around the Fe atom and corresponds to the SL component measured by eMS, confidently assigned to the substitutional Fe on Ti sublattice site in defect-free cubic lattice environment. In Fig.5(b), the implanted Fe atom takes the Ti lattice site which is bonded only to four co-planar N atoms, with two vacant N sites (3´ and 4´), perpendicularly aligned out-of-plane. This breaks the octahedral space-symmetry of the electron density distribution around the Fe atom, thus creating an appreciable ∆E0, in line with the hyperfine parameters of the component DB3, which counts for ~4% of the total spectral intensity at RT as shown in Fig.2(b).

However, as shown in Fig.2(b), it is surprising to observe that the area fraction/intensity of DB3 first increases from ~4% at 440 K to ~40% at 620 K, then reduces to 0% above 813 K. Corresponding changes in the area fraction/intensity of the SL component are also observed, but in the opposite direction. This points towards a temperature-dependent dynamic site-exchange between the occupied and the vacant N lattice sites in the TiN cubic structure. This can be explained in two possible ways, i.e. 1) the lattice N atoms become mobile and diffuses from occupied lattice site towards the vacant site, or 2) the implanted $^{57}$Mn/$^{57}$Fe probe atoms have a higher tendency to be trapped into the lattice defect area with
$V_N$ upon the lattice cascade damage, within the 90 s lifetime of $^{57}$Mn atoms in the temperature range of 540-620 K. With temperature increasing further to 710 K and above 813 K, due to the high mobility of nitrogen interstitials, which finally fill up the nitrogen vacancies, thus resulting in the increasing of SL at the reduction of DB3. We try to discuss these two possibilities in more details as the following.

Based on the theoretical simulation results from the literature [37] [38] [39] and our sample growth conditions [27], we know that:

N atom difuses significantly faster than the metal (Ti) atom and is thus expected to move by the vacancy ($V_N$, octahedral sites) diffusion mechanism in rock-slat cubic structure of TiN [40]. This means that the diffusivity of the N lattice atom is linked to the diffusion of $V_N$. $V_N$ and $N_I$ are regarded as the primary point defects in TiN. First-principles calculations [37] [38] found that diffusion of $V_N$ and $N_I$ are activated at different temperatures in a range of several hundreds of degrees, and are related to the interactions and migration of N point defects. The migration activation energy of $V_N$ is as high as 3.8 eV. The large barrier indicates that $V_N$ diffusion is activated only at very high temperatures. This practically means that the $V_N$ is stationary in the experimental temperature range in our case.

In contrast to $V_N$ vacancies, $N_I$ tends to form $N_I$ pair complexes in several stable configurations. $N_I$ migration is relatively facile, tend to form low energy split-configurations with stretched N-N bonds with a substantial binding energy of 0.55 eV aligning along [111] and [10\overline{1}] crystal directions, the latter is the minimum energy migration path. The calculated diffusion barriers ($E_d$) for isolated $N_I$ and $N_I$ pairs along [10\overline{1}] directions are 1.3 eV and 2.0 eV, respectively. (These are very reasonable numbers for interstitial defects). This relatively low $E_d$ value indicates that $N_I$ diffusion can be activated at much lower temperatures than $V_N$ [37], which may explain that the proportional changes of the SL and DB3 components can happen in the medium temperature range in our experiment.

Further study on diffusion of N vacancy and N self-interstitial point defects in TiN using ab initio and classical molecular dynamics (AIMD and CMD) simulations [39] confirmed that the most stable self-interstitial $N_I$ position in TiN is a split-bond configuration formed with nitrogen lattice atoms. This can be treated as a $N_2$ dimer centered at an anion lattice site ($N_I$-N$_{exc}$, where N$_{exc}$ refers to the lattice N atom pairing with $N_I$) with a N-N distance of 1.1 Å, which is about one third of the equilibrium N-N lattice distance ($\sim$3 Å) in TiN. After several random rotations around the $N_I$-N$_{exc}$ center of mass, which is in the proximity of the original N lattice site, the $N_I$-N$_{exc}$ bond breaks and one of the two N atoms permanently migrates to a neighboring anion site by passing through metastable eightfold-coordinated
tetrahedral positions, thus forming a Ni-V pair (Frenkel pair). This process yields temperature dependent Ni diffusion coefficients \(D_i(T)\) with an exponential pre-factor \(A_i = 7.28 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}\) and activation energy \(E_{i}^\prime = (1.17 \pm 0.13) \text{ eV}\). As for \(V_N\), it moves along [110] directions between neighboring N sites with much less mobility, yielding diffusion coefficients \(D_V(T)\) with an exponential pre-factor \(A_V = 3.89 \times 10^{-1} \times 10^{-1} \times 10^{-1} \times \exp[-3.65 \pm 0.23] \times 11604/\Delta T]\) and activation energy \(E_{V}^\prime = (3.65 \pm 0.23) \text{ eV}\). Based on equation (4) in Ref. [39], a general expression for the temperature dependent diffusion coefficients of Ni and \(V_N\) as follows:

\[
D_i(T) = 7.28 \times 10^{-4} \times \exp[-1.17 \pm 0.13] \times 11604/\Delta T
\]

\[
D_V(T) = 3.89 \times 10^{-1} \times 10^{-1} \times \exp[-3.65 \pm 0.23] \times 11604/\Delta T
\]

Based on the above equations, the diffusion coefficient and diffusion length within the lifetime of the Mn atom (90 s) of \(N_i\) and \(V_N\) at various annealing temperatures of the TiN thin film during eMS measurement can be calculated and listed in Table 3.

Table 3: Nitrogen self-interstitial (Ni) and nitrogen vacancy (\(V_N\)) diffusion coefficient and diffusion length at various annealing temperatures of TiN thin film during eMS measurement.

<table>
<thead>
<tr>
<th>(T (K))</th>
<th>(N_i) Diffusion coefficient ((\text{cm}^2 \text{ s}^{-1}))</th>
<th>(V_N) Diffusion coefficient ((\text{cm}^2 \text{ s}^{-1}))</th>
<th>Diffusion length (Å) within the 90 s lifetime of the (^{57}\text{Mn}) atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>540</td>
<td>((0.3-79) \times 10^{-15})</td>
<td>((0.01-118) \times 10^{-35})</td>
<td>1.6-27</td>
</tr>
<tr>
<td>620</td>
<td>((0.1-46) \times 10^{-13})</td>
<td>((0.01-155) \times 10^{-30})</td>
<td>9.9-204</td>
</tr>
<tr>
<td>710</td>
<td>((0.2-17) \times 10^{-12})</td>
<td>((0.05-516) \times 10^{-27})</td>
<td>46-389</td>
</tr>
</tbody>
</table>

Table 3 shows that at all temperatures, \(N_i\) diffusion coefficients are much larger than \(V_N\) by many orders of magnitude. This confirms that at the given annealing temperatures, \(V_N\) can be treated as stationary, whereas \(N_i\) is highly mobile.

Spontaneous formation and dissociation of \(N_i-V_N\) Frenkel pairs in a defect-free TiN is thermodynamically possible [39] and can be a perfect explanation on the conversion of SL to DB3 in our case. However, dynamically speaking, the probability of such event seems very rare with consideration that the annealing temperatures we used are far below the melting temperature of TiN. Therefore, some other factor is needed to support that the probability of spontaneous formation and annihilation of \(V_N\) under our experimental conditions during the 90 s lifetime of Mn atom is high enough to explain our data.
concerning the conversion of SL to DB3 in the temperature range of 540-620 K. Here we propose that the extra factor is the pre-presence of isolated N\textsubscript{i} in the lattice vacancy-free TiN. Indeed, as shown in Table 2, the hyperfine parameters for component \#1 (SL, Fe\textsubscript{s}) and component \#9 (Fe\textsubscript{c}-N\textsubscript{i}) are very similar. This means that there is a portion of (Fe\textsubscript{c}-N\textsubscript{i}) component hidden in the SL (Fe\textsubscript{s}) component, which is not distinguishable by eMS. The as-deposited TiN film in our case has lattice parameters around 4.248 Å, \(\sim 0.5-0.7\%\) larger than the lattice constant of stoichiometric cubic structured TiN (\(a = 4.242\) Å). This indicates that the concentration of N\textsubscript{i} in the thin film is apparently higher than the one used for the CMD and AIMD simulations (which assume \(a = 4.242\) and N\textsubscript{i} \(\sim 1\%\) of the total number of N atoms) [39]. There was also experimental evidence that the low-energy ion deposition like DC-magnetron sputtering can create N\textsubscript{i}[41]. As shown in Table 3, owing to its low diffusion barrier and high diffusion coefficient, this portion of N\textsubscript{i} can be thermally mobilized as the temperature increases from 540 K to 620 K and may create new defect structures in TiN. As it has been discussed above, the N\textsubscript{i} tends to form a strong N-N bonds with the nitrogen lattice atoms in low energy split-configurations and diffuses through the energy minimum migration path along the [10\overline{1}] direction. It is plausible that during migration, before each jump, the isolated N\textsubscript{i} temporarily bonds with the nearest lattice N atom (N\textsubscript{exc}) as a metastable N\textsubscript{exc}-N\textsubscript{i} complex aligning along the [10\overline{1}] direction. The N\textsubscript{exc}-N\textsubscript{i} complex has binding energy of 0.55 eV and bond length of 1.1 Å, about one third of the equilibrium N-N lattice distance (\(\sim 3\) Å) in TiN [39]. This is quite a strong/tight bond comparing with the N-Ti bond in TiN. This means that the lattice N in the N\textsubscript{exc}-N\textsubscript{i} pair would be temporarily carried away from its equilibrium lattice site in TiN cubic lattice as migration of N\textsubscript{i}. Each formation of a N\textsubscript{exc}-N\textsubscript{i} bond would create a metastable V\textsuperscript{V\textsubscript{N}} at the original N lattice site. In most cases, the N\textsubscript{exc} and V\textsuperscript{V\textsubscript{N}} recombines within a fraction of ns; \(\sim\)half of these processes result in the exchange of two nitrogen lattice atoms and creation of extra V\textsubscript{N}. This is similar to a chain reaction of spontaneously formation/dissociation of (N\textsubscript{exc}-N\textsubscript{i}) pair accompanied by V\textsubscript{N} creation/refilling, catalysed by the pre-presence of N\textsubscript{i} species as the follow:

\[
N_{\text{lattice}} + N_i \xrightarrow{\text{exc}} (N_{\text{exc}} - N_i)_{\text{pair}} + V_N^{'} \xrightarrow{\text{exc}} 2 (N_{\text{exc}} - N_i)_{\text{pair}} + V_N^{'} \xrightarrow{n} n (N_{\text{exc}} - N_i)_{\text{pair}} + n V_N^{'}
\]

This equals a conversion of SL to DB3 with probability of \(\sim 50\%\) [39] as N\textsubscript{i} migrates along [10\overline{1}] direction from one TiN cubic unit cell to the next unit cell in the temperature range of 540 K to 620 K. The probability increases exponentially with temperature. Above 700 K, the migration length of N\textsubscript{i} within the lifetime of the \(^{57}\text{Mn}\) atom (90 s) reaches 46 Å-400 Å distance, which is comparable to the typical grain size of the TiN thin film. With this diffusion length, the excess N\textsubscript{i} inside the crystal grain could migrate all the way to the V\textsubscript{N} sites or to the surface of the grain boundaries to be annihilated as N\textsubscript{2}. 
The second possibility is that the implanted $^{57}\text{Mn}^{/57}\text{Fe}$ atoms preferably stop more in the $V_N$ area than the defect-free area, upon the implantation-induced structural cascade damage in the temperature range of 540 - 620 K, thus leading to a higher portion of DB3 to be probed by eMS during the 90 s lifetime of $^{57}\text{Mn}$ atoms. With temperature increasing, the damage sites are annealed, and $N_I$ diffuses to fill the $V_N$ sites, which leads to a recovery of the SL component and a final disappearance of the DB3 component. However, as confirmed by the quenching results in Fig.3, there is no significant lattice damage to be found in eMS as a result of $^{57}\text{Mn}$ implanting from RT to 450 K. It is unlikely that more cascade damage would occur at 540 - 620 K. The minor components shown in the eMs were related to the intrinsic structural defects in the sample. Therefore, attributing the increase of DB3 to the preferable location of $^{57}\text{Mn}^{/57}\text{Fe}$ atoms in the cascade damage area is less supportable by the present data.

In summary, from both the experimental and the theoretical points of view, there exist mobile $N_I$ atoms in the defect-free bulk-like phase of TiN thin films. The conversion of the SL component to the DB3 component can be the result of a diffusion of $N_I$ coupled with the temporary creation of metastable $V_N$. With temperature increasing to 700 K and above 810 K, $N_I$ diffuses to fill the intrinsic $V_N$ sites in the bulk, or all the way to the grain boundary and surface of the thin film to be released as $N_2$. This leads to a recovery of SL component and the final disappearance of the DB3 component. The overall process concerning the conversion of SL and DB3 based on the diffusion of $N_I$ and refilling of $V_N$ is schematically illustrated in Fig.5.
Fig. 5: Schematic illustration of the local lattice configurations of substitutional Fe, and the conversion of SL and DB3 in the experimental temperature range (303-810 K). In (a), the $^{57}$Fe atom occupying a Ti lattice site bonded by six fully occupied nearest N atoms (1, 2, 3, 4, 5 and 6) represent component SL. Whereas in (b), among the six nearest N sites, the two N sites (3’ and 4’) which are arranged at 180º relative to each other, are vacant and represent component DB3. In (c), additional N, located at the cubic unit cell center A of TiN, is shown with the possibility to form a stretched (N exc-N) pair like a N$_2$ dimer with the lattice N atom at site 9 or 10 and diffuse further away along the [101] direction (shaded in color) as shown in (d and e), which is the most stable configuration and lowest energy migrating path of N$_i$[37]. At medium temperatures 540 K - 620 K, transition among configurations from (c) to (d), (e) and (b) by the formation of (N exc-N) pairs and creation of metastable nitrogen vacancy (V N) is more likely. With temperature increasing from 710 K to above 810 K, with further diffusion of (N exc-N) pairs, direct transition from (e) to (a) by healing metastable nitrogen vacancy (V N) with N exc and filling of intrinsic V N with N$_i$ is feasible. The related half unit cell structures of TiN cubic are shown in (f)-(j), respectively. The step-wise transition from (c) to (d) and back to (b) and (a) is detailed in (k). Solid green, yellow and black circles represent Ti, N lattice atoms and substitutional $^{57}$Fe atoms on Ti lattice sites, respectively. Filled dotted and void solid yellow circles represent N$_i$ and V N, respectively. Note: the $^{57}$Fe should be treated as $^{57}$Mn in the context of immediate interaction of implanted atoms with the local crystal structures upon implantation. The bottom block shows the process by which V N was temporarily created as a result of N$_i$ diffusing through the lattice defect-free area in a form of (N exc-N) pair. This explains the area conversion between components SL and DB3 in eMS in the temperature range of 540 - 620 K.

4.2.2. Site assignments for components DB1 and DB2

Fig. 6 illustrates the two configurations of Fe$_i$ at the centre of a TiN cubic structure with V Ti and V N, respectively, in the grain boundary region. On account of the cubic structure, growth of TiN is generally controlled by the competition between the temperature-dependent fast lateral growth rate of the (200) oriented grains and the large geometric growth rate of the (111) oriented grains. In our case, the growth in (200) orientation is found favourable at 400 °C because of the epitaxial relationship with the substrate crystal structure [27]. Therefore, as shown in Fig.6(a), the (110) plane, which is a common side for both the (200) and (111) orientations, is chosen to represent the grain boundary. Based on the experimental evidence, oxygen can be introduced from remaining O$_2$ in the vacuum chamber (1.3 × 10$^{-4}$ Pa) during deposition or exposure of the sample to air, and then reacts with Ti in TiN at the grain boundary and the surface to form oxides [17], [27], [42]. An ultrathin oxide passivation layer can be formed at an intermediate temperature and low partial oxygen pressure, where the temperature is high enough for the V Ti, created upon initial oxidation, to diffuse away from the TiN/oxide interface, but too low to allow any substantial relaxation of the initially formed oxide islands into pseudo-amorphous and more reactive structures. The oxygen pressure is low enough to allow the oxidation to reach equilibrium. Under these conditions, the oxide layer formed is structurally ordered. It consists of -O-Ti- rows and represents a (1×1) surface unit cell, where vacancy segregation from bulk to the TiN/oxide interface is strongly
inhibited, and for the same reason, further oxide growth into the bulk is inhibited since it would require overcoming a high-energy barrier [43].

Under the conditions in which the TiN film of this study was grown, stored and post-annealed at temperature ranging from RT to 813 K, the formation of an ultrathin oxide passivation layer at the grain boundary and the surface is unavoidable. Theoretical modelling of surface oxidation of TiN [43] demonstrated that in the case of TiN (100), Ti vacancies form spontaneously during the initial oxidation reactions and remain underneath the resulting reconstructed oxides which form structurally stable -O-Ti-bridging rows, and has been observed experimentally [44] [45].

Based on the theoretical study and experimental results in Table 2, considering the magnetron sputtering thin film growth conditions, which tend to produce a TiN thin film with appreciable amount of grain boundaries (2%-7%) and ultrathin-surface-oxidation as mentioned above, we assign DB1 to the FeI located at the center of a cubic unit cell of TiN with V_{Ti} (#12 in Table 2) at the grain boundaries owing to oxidation of Ti atoms upon adsorption of O atoms. The process is schematically illustrated in Figs.6(b) and (d). Fig.6(b) illustrates the FeI in the center of the TiN cubic unit cell with a V_{Ti} (position 4) at the grain boundary, where the nearest-surface Ti atoms in TiN cubic structure close to the grain boundary have moved from the original positions (1, 2 and 3) outward to the boundary surface positions (1’, 2’ and 3’) in TiO_{4} tetrahedral structure underneath the -O-Ti- bridging rows as a result of oxidation of surface Ti atoms of TiN [43]. This enhances the distortion of the cubic symmetrical surrounding of the V_{Ti}. The FeI, which is either due to the implantation or the recoil-induced relocation of Fe (<E_{R} > = 40 eV, E_{R,Max} = 93 eV), most likely stops at the grain boundaries. Comparing to the bulk phase, the FeI at the grain boundary not only experiences the distorted electron field, caused by the V_{Ti} in the cubic lattice, but also the highly disordered immediate crystal structure at the grain boundary. Therefore, it is reasonable that
the experimental value $\Delta E_Q$ of DB1 appears to be larger than the calculated value which is obtained by assuming the Fe$_i$ at the center of the TiN lattice cubic in the bulk phase.

Likewise, DB2 can be assigned to interstitial Fe$_i$ in the center of a TiN cubic with V$_N$ (#11 in Table 2) at the grain boundaries as shown in Figs.6(c) and (e). Owing to the presence of unbonded N sites (dangling N bonds) located at the TiN/oxide interface in the proximity of V$_{Ti}$, it is thermodynamically favorable [43] and plausible that an initial release of N atoms as N$_I$ would take place at the TiN/oxide interface shortly after formation of an ultrathin oxide layer on TiN thin film (at RT) as shown in Fig.6(c). Many reports agree that a certain amount of N$_2$ remains trapped in the uppermost part of the oxidized layer formed [46] [47] [48] [49]. Only with increasing temperature [47] or with the growth of oxide layers [48] N$_I$ is completely released from the surface, either as N$_2$ or by formation of NO gas [41] [50] [51]. With the possibility of excess N$_I$ trapped at the grain boundaries [50], in contrast to the isolated V$_N$ in the bulk structure, V$_N$ at a grain boundary is likely to form a complex with N$_I$. This can explain that the measured $\Delta E_Q$ of DB2 appears to be smaller than the calculated value due to the possible refilling of V$_N$ by N$_I$ at the grain boundary.
Fig. 6(c) illustrates the Fe\textsubscript{I} located at the centre of the TiN cubic structure with a V\textsubscript{N} (position 4) near the grain boundary where the N\textsubscript{I} is shown in a metalstable structure with tendency to bond to V\textsubscript{N} site or to be released as N\textsubscript{2} or NO gas upon annealing [47] [51]. In this configuration, the unbalanced electron density caused by V\textsubscript{N} in the TiN unit cell experienced by the Fe\textsubscript{I} can be dynamically balanced to a certain extent by the nearby N\textsubscript{I} at the grain boundaries. Therefore, it is reasonable that the actually measured $\Delta E_Q$ value of DB2 appears to be smaller than the calculated one, which assumes that the Fe\textsubscript{I} is located in the N\textsubscript{I} -free cubic centre of the TiN in the bulk phase.

Finally, as temperature increases, the structure defects at grain boundaries can be annihilated. Therefore, as shown in Fig. 2(b), the area fractions of DB1 and DB2 decrease with temperature.

**Conclusions**

With $^{57}$Fe eMS by dilute implantation of $^{57}$Mn and theoretical calculations, we obtained the atomic scale lattice defect structures in an ultrathin epitaxial TiN film grown on MgO (100), which have been overlooked by other macroscopic analysing tools [27]. Most $^{57}$Fe atoms were found to substitute Ti in the TiN lattice adopting the valence state 2\textsuperscript{+}, with the rest located at the grain boundaries as interstitials. A small percentage (~4\%) of V\textsubscript{N} is detected in the bulk-like crystalline grains in the TiN thin film. Based on the theoretical predictions and the experimental conditions, it is most likely that a small portion of N\textsubscript{I} exists inside the crystalline grains in the TiN thin film, which can be thermally activated and diffuses in a form of N\textsubscript{2} dimer-like N-N pair to promote the N\textsubscript{I}-V\textsubscript{N} pair formation inside the crystal grains, thus leading to a dynamic site-exchange between the lattice-N atom and the V\textsubscript{N} in the temperature range 540-620 K. Above 813 K, the compensation of V\textsubscript{N} with N\textsubscript{I} inside the crystalline grains or annihilation of N\textsubscript{I} at the grain boundaries are more favourable. Furthermore, the results enable identifying the specific structural defects at the grain boundaries, which are consistent with experimental observations and theoretical modelling of the atomic scale oxidation of TiN at the surface. V\textsubscript{Ti} is only detected at the TiN grain boundaries at RT, which can be annealed out at temperature above 813 K. There is no strong evidence of ferromagnetism resulting from dilute implantation of $^{57}$Mn/$^{57}$Fe or due to intrinsic structural defects in the film. This work demonstrates that emission Mössbauer spectroscopy, assisted by theoretical calculations, is a powerful tool to study the defects in TiN nanostructures as well as the possibility of defect-induced or dilute-ferromagnetism on an atomic scale.

**Acknowledgments**
This work was supported by the European Union Seventh Framework through ENSAR (Contract No. 262010). B. Qi, H. P. Gislason, S. Ólafsson and F. Magnus acknowledge support from the Icelandic Research Fund (Grant No. 110017021-23). A. Tarazaga Martín-Lueugo and A. Bonanni acknowledge the support by the Österreichische Forschungsgesellschaft – FFG (P841482), the Austrian Science Foundation – FWF (P26830) and the European Research Council – ERC (grant 227690). We also acknowledge the support provided by the RILIS and technical teams at ISOLDE-CERN and by the Federal Ministry of Education and Research (BMBF) through the grants 05K16PGA and 05K16SI1.

References


Highlights:

- $^{57}$Fe Mössbauer spectroscopy at truly dilute level ($<10^{-3}$ at\%) is applied.
- An ultrathin epitaxial TiN thin film structure is studied.
- Theoretical calculations are provided to assist the analysis of the experimental measurement results.
- The structure and mobility of the lattice defects in the TiN film are probed at atomic scale.