On the chemical composition of TiAlN thin films - Comparison of ion beam analysis and laser-assisted atom probe tomography with varying laser pulse energy

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**ABSTRACT**

We compare the chemical composition of TiAlN thin films determined by ion beam analysis and laser-assisted atom probe tomography (APT). The laser pulse energy during APT was increased subsequently from 10 to 20, 30, 40, 50, 100 and 200 pJ within a single measurement, covering the range that is typically employed for the analysis of transition metal nitrides. The laser pulse energy-dependent Ti, Al and N concentrations were compared to ion beam analysis data, combining Rutherford backscattering spectrometry (RBS) and elastic recoil detection analysis (ERDA) with the total measurement uncertainty of 2.5% relative deviation. It can be learned that the absolute N concentration from APT is underestimated by at least 5.5 at.% (up to 8.2 at.%), and the absolute Al concentration from APT is overestimated by at least 4.5 at.% (up to 6.2 at.%), whereas absolute Ti concentration values are for both techniques in good agreement with maximum deviations < 2 at.%

1. Introduction

Most commonly the chemical composition of thin films is determined by energy dispersive X-ray spectroscopy (EDX), wavelength dispersive X-ray spectroscopy (WDX) and X-ray photoelectron spectroscopy (XPS). While these techniques are available in most research environments, the composition data quality is affected by several well known measurement technique-inherent limitations. These limitations are briefly discussed in the following for thin films that contain so called light elements and TiAl(O)N serves as a model system for this discussion. Quantification of light elements is challenging due to their low photon energies which lead to significant (matrix-dependent) absorption of generated X-rays within the specimen as well as within the spectrometer [1]. Furthermore, the measurement accuracy of EDX is limited by overlaps of K-shell transitions as N and O ($E_{N-Kα} = 0.392\text{keV}, E_{O-Kα} = 0.525\text{keV}$) with the L-shell transition of Ti ($E_{Ti-Lα} = 0.452\text{keV}$). These overlaps can result in systematic uncertainties of up to 40% relative deviation of Ti and N concentrations [2].

EDX is a time-consuming technique since many calibration samples need to be analyzed. Therefore, a combination of EDX (Ti, Al) and WDX (N, O) has been proposed for TiAlON thin films [3]. XPS is characterized by a measurement depth of few nanometers and is therefore commonly used for surface characterization rather than measuring ‘bulk’ compositions [4,5]. In this context it was recently shown that the extent of surface composition modification of TiN thin films due to atmosphere exposure after thin film growth exhibits a strong dependence on the venting temperature [6].

Chemical quantification without utilization of standard samples (and hence calibration) can be realized by ion beam-based analysis techniques such as Rutherford backscattering spectrometry (RBS) and time-of-flight elastic recoil detection analysis (ToF-ERDA). Relative systematic uncertainties of ToF-ERDA for N are typically in the order of ± 10% [7]. The origin are systematic uncertainties due to detection efficiencies < 1 for light elements and the detection efficiency is dependent on the probability of electron emission as well as detection in the ToF detectors (supplementary material of [8]). Since quantitative
Composition analysis by ToF-ERDA is based on time and energy coincidence spectra. Light ions will not be detected if electrons are not emitted upon passing the ToF setup. The uncertainty of RBS is dominated by counting statistics in the order of ±1% and it was recently shown for TiAlN that the combination of RBS and ToF-ERDA results in a total measurement uncertainty of ±2.5% relative deviation (supplementary material of [9]).

The characterization technique atom probe tomography (APT) offers spatially-resolved chemical composition analysis at the nanometer scale. Recent technical improvements, such as rapid detection electronics, large field of view and local extraction electrodes, paved the way for APT as a versatile tool for materials analysis [10,11]. The mass resolution is sufficient to separate the individual isotopes of all elements [12] and statistical tools allow to investigate the local distribution of constitutional elements [13]. It is well known that the chemical composition obtained by APT can be affected by the evaporation conditions, therefore, measurement parameter studies are required prior to analysis of new material systems [14].

The utilization of APT for characterization of TiAlN thin films has increased within the last decade and the first report showing APT data on the thermally-induced decomposition of magnetron sputtered TiAlN dates back to 2010 [15]. Cathodic arc evaporated (Ti0.41Al0.59)0.51N0.49 thin films were also quantified by APT: taking the statistic uncertainty into account, no change in the average concentration of APT specimens was determined after isothermal vacuum annealing at 900 °C for 2 h, while locally preferential N segregation from the TiAlN matrix to AlN- and TiN-rich regions was observed [16]. Further, nitrogen deficient (Ti0.52Al0.48)Ny powdered coatings [17] and thin films [18] were studied with respect to their thermal stability. While for powdered coatings the highest thermal stability was observed for y = 0.75 [17], a higher N concentration of y = 0.87 was suggested to be beneficial for the thermal stability of thin films [18]. These composition data were determined by APT and compared to ERDA for the (Ti0.52Al0.48)Ny powdered coating: N concentrations were 42.8 ± 0.6 (APT) and...
37.7 ± 1.8 at.% (ERDA), while Al concentrations were 26.9 ± 0.3 (APT) and 27.4 ± 0.8 at.% (ERDA) and Ti concentrations, estimated from the balance to Al, N and the impurity content (< 0.2 at.%), were 30.1 at.% (APT) and 34.7 at.% (ERDA) [17].

Accurate and precise chemical composition data is of paramount importance for meaningful thin film materials science investigations as well as for the design of thin films with tailored properties. Absolute concentrations of the constitutional elements define the defect structure which is correlated with phase formation [19,20], thermal conductivity [21], resistivity [22], elastic properties [23] and thermal stability [24]. In the present work we compare the chemical composition of TiAlN thin films determined by ion beam analysis and laser-assisted APT, where field evaporation is caused by the electric field as well as by thermal energy input from the laser [25]. Hence, we investigate the effect of thermal energy input on the absolute concentration values due to variations in the laser pulse energy.

2. Experimental details

Previously, close-to-stoichiometric TiAlN was grown from a TiAl target by high power pulsed magnetron sputtering in an Ar/N₂ atmosphere employing gas phase combinatorics. The chemical composition of (Ti₀.₂₅₅Al₀.₂₃₅)(N₀.₅₀₅O₀.₀₀₅) has been reported based on combination of RBS and ERDA (the experimental details regarding synthesis and ion beam analysis can be found in Ref. [9]). This close-to-stoichiometric thin film was studied in the present work by three-dimensional APT using a Cameca local electrode atom probe 4000X HR. Field evaporation was triggered by laser pulses on top of a DC standing voltage. The pulse frequency and base temperature were set constant at 250 kHz and 60 K, respectively, and the average detection rate was 5 ions per 1000 applied laser pulses. The pulse energy of the ultraviolet laser was increased subsequently from 10 to 20, 30, 40, 50, 100 and 200 pJ within a single measurement. For each laser pulse energy value 4 × 10⁶ ions were acquired, resulting in a total ion count of 28 × 10⁶. Data reconstruction of each pulse energy segment was done by employing the IVAS 3.8.0 software package. The amount of multiple detection events was extracted by using the software EPOS which was developed at the Institute of Physics (IA) of RWTH Aachen University.

Ranging of the mass spectrum is a critical step towards obtaining accurate and precise chemical compositions. For each peak the mass-to-charge ratio of the maximum intensity was identified (e.g. 13.494 Da for Al²⁺) and compared to the peak onset from the background (e.g. 13.450 Da for Al²⁺). The range was then defined symmetrically by the difference of these mass-to-charge state ratios (e.g. 13.450 to 13.538) in order to minimize the contribution of thermal tails. Besides Ti, Al and N, impurities of O (approximately 1 at.%) and traces of C, Ar and Ga (< 1 at.%) were identified.

Needle-like atom probe specimens were prepared by focused ion beam (FIB) techniques [26], see Fig. 1, in a FEI Helios Nanolab 660 dual-beam microscope utilizing Ga ions at 30 kV acceleration voltage. Specimen preparation was finished by cleaning the tip at a voltage and current of 5 kV and 40 pA, respectively. The analyzed atom probe specimen exhibited a final tip radius of 30 nm and a shank angle of 15°, Fig. 1 h).

Moreover, a thin lamella was extracted in growth direction using FIB for morphological characterization by scanning transmission electron microscopy (STEM) using a STEM III detector in bright field mode.

3. Results and discussion

3.1. Crystal structure and morphology

The investigated thin film exhibited a single phase cubic structure (space group Fm₃m, NaCl prototype) [9] and a columnar growth morphology, which is evident from Fig. 2. The column width is on the order of 100 to 200 nm and, thus, larger than the analyzed volume of

![Fig. 2. STEM micrograph of the TiAlN thin film and three representative APT reconstructions for comparison of the analyzed volume to the columnar width.](image)

APT as indicated by three representative APT reconstructions.

3.2. Laser pulse energy-dependent absolute concentrations

Concentration values of Ti, Al and N are presented as a function of laser pulse energy in Fig. 3 and the sampling size for each pulse energy is 4 × 10⁶ ions. The statistic uncertainty of APT concentrations (count rate error [27]) is < 0.1 at.%. The Ti, Al and N concentration changes induced by increasing the laser pulse energy from 10 to 50 pJ are minute, but significantly larger than the uncertainty due to counting statistics: measured average concentrations in this energy range for Ti, Al and N are 25.6 to 26.0 at.%, 28.0 to 28.2 at.% and 44.7 to 44.9 at.%, respectively. Higher laser pulse energies of 100 and 200 pJ result in an increase of Ti to 26.3 and 27.1 at.%, an increase of Al to 28.6 and 29.6 at.% and a decrease of N to 43.8 and 42.3 at.%. Hence, the maximum laser pulse energy-induced absolute composition changes for Ti, Al and N are 1.3, 1.8 and 2.5 at.%, respectively.

3.3. Comparison of RBS/ERDA and APT data

Corresponding Ti, Al and N concentrations of 25.5 ± 0.6, 23.5 ± 0.6 and 50.5 ± 1.3 at.%, respectively, were obtained by combination of RBS and ERDA (referred to as RBS/ERDA) and are also
indicated in Fig. 3 where the line width represents the total measurement uncertainty of 2.5% relative deviation (supplementary material of [9]). It can be learned that the absolute N concentration from APT is underestimated by at least 5.5 at.% (20 pJ) and up to 8.2 at.% (200 pJ), while the absolute Al concentration from APT is overestimated by at least 4.5 at.% (20 pJ) and up to 6.2 at.% (200 pJ). Absolute Ti concentration values are for both techniques in good agreement with maximum deviations < 2 at.%.

Since it is evident from Fig. 2 that the APT analysis volume is significantly smaller than the column width, three specimens were measured at identical laser pulse energy of 30 pJ to compare chemical compositions of different thin film regions. Thereby, concentration ranges of 25.6 to 26.6 at.% Al and 27.9 to 28.4 at.% N were obtained for Ti, Al and N, respectively. Thus, it is evident that the compositional deviation between ion beam analysis and APT is substantially larger than the count rate error of APT as well as composition fluctuations originating from different thin film regions. It can be further summarized that the accuracy of APT is on the order of 5 to 8 at.% while the precision is approximately 1 at.% for the here performed measurements.

Expected contributions to the discrepancy between absolute elemental Ti, Al and N concentrations obtained by RBS/ERDA and APT are molecular ions, multiple detection events and preferential evaporation/retention of species with different evaporation fields. These effects are discussed below.

3.4 Molecular ions

Mass spectra are compared for laser pulse energies of 30 and 200 pJ in Fig. 4. It is evident that the chemical composition is to a large extent governed by elemental species (Ti\(^{2+}\), Ti\(^{3+}\), Al\(^{+}\), Al\(^{2+}\), Al\(^{3+}\), N\(^{+}\)). However, independent of the laser pulse energy, there is also a significant fraction of molecular ions (AlN\(^{2+}\), N\(^{2+}\), TiN\(^{2+}\), TiN\(^{3+}\)). Constituting approximately 30% of the total mass spectrum. Quantitative APT analyses of nitrides often result in N-deficient compositions, e.g. for (system-dependent) laser pulse energies of > 10 pJ (Cameca LEAP 4000X HR) [28] or ≥1.2 nJ (Cameca LAWATAP) [29]. Recently, it has been reported by Schramm that the peak at 14 Da (attributed to N\(^{2+}\) in Fig. 4) contains a contribution of N\(^{2+}\) which may be estimated from a characteristic N\(^{2+}\) peak at 14.5 Da and a peak overlap correction was suggested (without providing mass spectra) [30]. It is evident from the inset in Fig. 4 that no peak at 14.5 Da can be identified. In addition, the measured \(^{14}\)N\(^{+}\) and \(^{15}\)N\(^{+}\) abundancies are with 99.388% and 0.612% (30 pJ laser pulse energy) very close to the natural abundancies of 99.636% and 0.364% [31].

In the following two hypothetic N\(^{2+}\) contributions to the peak at 14 Da are considered for the mass spectrum with 30 pJ laser pulse energy. Assuming a N\(^{2+}\) contribution of 100%, concentrations of 22.9 at.% Ti, 27.3 at.% Al and 49.8 at.% N would be obtained. Thus, this hypothetical N concentration would be in good agreement with ion beam analysis data, while Ti would be underestimated by 2.6 at.% and Al overestimated by 3.8 at.%. In case of a hypothetical N\(^{2+}\) contribution of 50%, concentrations of 24.1 at.% Ti, 28.8 at.% Al and 47.1 at.% N would be obtained. Hence, Ti would be in good agreement with ion beam analysis data, while N would be underestimated by 3.4 at.% and Al would be overestimated by 5.3 at.%.

Consequently, taking the measured isotope ratio \(^{28}\)N/\(^{29}\)N into account, the 14.5 Da peak intensity of approximately 200 and 100 counts above the background signal is corrected for hypothetic N\(^{2+}\) contributions to the peak at 14.5 Da of 100 and 50%, respectively. These expected values are indicated by the open square (100% N\(^{2+}\) contribution) and open circle (50% N\(^{2+}\) contribution) within the inset of Fig. 4 and both would be clearly visible, if present. Since there is no peak visible, there is no evidence for the presence of N\(^{2+}\) and, hence, no reason to correct for the presence of N\(^{2+}\).

Furthermore, it is well known that N\(^{2+}\)-carrying molecular ions may dissociate during flight and that the neutral fragment may not be ionized as the electric field is too weak [32]. This dissociation mechanism results in neutral fragments which can not be detected with a micro-channel plate detector. Moreover, at a field strength of 60 V nm\(^{-1}\) the probability for double ionization of N\(^{2+}\) is < 1/10^4 [32]. As discussed in section 3.6, a maximum electric field strength of 40 V nm\(^{-1}\) is estimated in the present work, rendering the probability to form N\(^{2+}\) ions < 1/10^9 [32]. As we operate at field strengths where the formation of N\(^{2+}\) is highly improbable and since we observe no evidence for the presence of N\(^{2+}\) from the peak at 14.5 Da, the 14 Da peak is associated with N\(^{+}\).

3.5 Multiple detection events

The arrival of multiple species within a single pulse (multiple detection events) can be explained by a strong correlation in time and
space between field evaporated atoms [33]. Compared to metallic materials, ions tend to evaporate as molecular ions to a much larger extent in case of nitrides [34] and the dissociation of these molecular ions (see discussion in section 3.4) contributes to multiple detection events. As a consequence a significant amount of abundant ions can not be registered due to pile-up on the detector [35]. Hence, it appears reasonable that multiple detection events affect the measured composition [33]. However, in the present study the amount of such events was observed to decrease from approximately 56 to 41%, when comparing laser pulse energies of 10 and 200 pJ (Fig. 3), while the N concentration difference between APT and RBS/ERDA increased from 5.1 to 8.2 at.%. Therefore, it is unlikely that multiple detection events dominate the reduction in N content, when increasing the laser pulse energy from 10 to 200 pJ.

3.6. Preferential evaporation/retention

Charge state distributions of Ti$^{2+}$, Ti$^{3+}$, Al$^{+}$, Al$^{2+}$ and Al$^{3+}$ as well as charge state ratios Ti$^{3+}$/Ti$^{2+}$, Al$^{+}$/Al$^{2+}$ and Al$^{3+}$/Al$^{2+}$ are shown in Fig. 5. The increase in laser pulse energy from 10 to 200 pJ results in a decrease of Ti$^{3+}$/Ti$^{2+}$ and Al$^{3+}$/Al$^{2+}$ ratios from 0.48 and 0.14 to 0.20 and 0.07, respectively, while the Al$^{+}$/Al$^{2+}$ ratio increases from 0.17 to 0.55. Based on post-ionization theory [36] so called Kingham curves were derived for many metals in order to predict the probability of post-ionization as a function of electric field strength [37]. These predictions were verified experimentally for metals [38]. Despite significant differences in the field evaporation of metals and nitrides, the measured charge state distributions are used to estimate the electric field strength. Charge state ratios of Ti$^{3+}$/Ti$^{2+}$ indicate an electric field range of approximately 38 to 39 V nm$^{-1}$. This range is in good agreement with a reported electric field value of approximately 40 V nm$^{-1}$ for TiN [39]. In contrast, single-, double- and triple-ionized Al is present in all investigated specimens. While the charge state ratios of Al$^{3+}$/Al$^{2+}$ suggest an electric field range of 39 to 40 V nm$^{-1}$, significantly lower values in the range of 26 to 28 V nm$^{-1}$ are obtained for double ionization of Al from the charge state ratios of Al$^{+}$/Al$^{2+}$. Therefore, it is speculated that Al may be preferentially evaporated which could explain the overestimation of Al concentrations by APT in comparison to RBS/ERDA.

Additionally, contributions of the electric base field as well as the thermal laser pulsing can be extracted from the charge state fractions. The fraction of Ti$^{3+}$ and Al$^{3+}$ reduces significantly upon increasing the laser pulse energy from 10 to 200 pJ. This reduction can be explained by an increased heat input at the specimen, which results in a lower electric base field under the assumption of an unchanged required evaporation field [40]. Thereby, the probability for triple ionization is lower in case of higher laser pulse energies.

4. Conclusions

We have compared the chemical composition of a close-to-stoichiometric TiAlN thin film by ion beam analysis and laser-assisted APT, varying the laser pulse energy in the range from 10 to 200 pJ within a single measurement. It can be learned that the absolute N concentration from APT is underestimated by at least 5.5 at.% (20 pJ) and up to 8.2 at. % (200 pJ) and the absolute Al concentration from APT is overestimated by at least 4.5 at.% (20 pJ) and up to 6.2 at.% (200 pJ), while absolute Ti concentration values are for both techniques in good agreement with maximum deviations < 2 at.%. The here presented comparative analysis clearly shows that absolute Al and N concentration values obtained by ion beam analysis deviate significantly to the APT data for the laser pulse energy range from 10 to 200 pJ. Underestimation of N is explained by the formation of neutral fragments upon dissociation of molecular ions during the flight, where the electric field is insufficient to induce ionization of the neutral fragment [32]. According to Gault et al. [32], the formation of double ionized N$_2$ is with an extrapolated probability of < 1/10$^9$ highly unlikely for the here estimated field strength of 40 V nm$^{-1}$. Overestimation of Al could be caused by preferential evaporation. The presented data emphasize that laser-assisted APT is a precise tool to quantify the chemical composition of TiAlN thin films, that lacks accuracy.
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