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# Transmission electron microscopy characterization of TiN/$SiN_x$ multilayered coatings plastically deformed by nanoindentation

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ABSTRACT

Plastic deformation of $TiN_{5\ nm}/SiN_{0.5\ nm}$ multilayers by nanoindentation was investigated by transmission electron microscopy in order to identify deformation mechanisms involved in film failure resulting from severe plastic deformation. The TiN layers exhibited a crystalline *fcc* structure with a [002] preferential orientation; further crystal growth was interrupted by the amorphous $SiN_x$ layers. After severe plastic deformation collective vertical displacement of slabs of several TiN/$SiN_x$-bilayers, which resulted from shear sliding at TiN/TiN grain boundaries, was observed. They are, together with horizontal fractures along the $SiN_x$ layers, vertical cracks under the indenter tip following the TiN grain boundaries and delamination from the substrate, the predominant failure mechanisms of these coatings. The deformation behaviour of these films provides an experimental support for the absence of dislocation activity in grains of 5 nm size.


## 1. Introduction

Titanium nitride was introduced in the early 1980s as protective coating material for cutting and forming tools. To enhance its hardness, coatings with nanosized grains are designed either in the form of nanocomposites, composed of crystalline TiN nanograins surrounded by an amorphous SiN matrix [1–5], which can be deposited by different techniques[6–10], or alternatively in the form of multilayers [11–15]. The nanoscaled multilayers are constituted by two hard transition metal nitrides with individual layer thickness of the order of several nanometers. Such coatings exhibit excellent properties like high hardness and high wear resistance [16–18], which depend critically on the thickness of the individual layers [18,19] as well as on the nature of the interface [20].

The most popular method to measure the hardness of coatings is nanoindentation [21], however it is a destructive method, which induces plastic deformation into the coatings, and allows thus to observe the occurring deformation mechanisms and the damages generated in the material. The knowledge of these mechanisms will help in a targeted design of coatings with better hardness properties. The deformation in nanocrystalline materials such as nanocomposites occurs by shear sliding at grain boundaries, grain boundary rotation and collective displacement of non-deformed nanocrystals [22–24] and as observed by Cairney et al. [25] via cracking at the nanocrystalline boundaries under local tension in a quasi-plastic manner. Moreover it has to be pointed out that in nanocomposites the grain size is too small to be deformed by dislocation activity [23].

The nanomultilayers built of alternating layers of *nc*-TiN and amorphous $SiN_x$ allow an independent variation of the single layer thickness and an unambiguous visualization of the amorphous phase, both as prepared and after being plastically deformed. The intercalating $SiN_x$ layers act as markers to help retrieve the original position of the multilayer segment prior to deformation. Such nanosized multilayers with alternating layers of TiN and $SiN_x$ were described by Chen et al. [26] with a hardness maximum found for a $SiN_x$ thickness of 0.5 nm. Another study on the hardening mechanism present in multilayered $Si_3N_4$/TiN coatings was performed by Xu et al. [27]. They found that the hardness of the multilayers is affected not only by the modulation period, but also by the layer thickness ratio and deposition temperature. These authors suggested that the alternating stress field caused by the mismatch of the thermal expansion coefficients of $Si_3N_4$ and TiN is one of the main reasons for the hardness enhancement in this multilayered system. Recently Söderberg et al. [12–15] investigated nanomultilayers of TiN and $SiN_x$ and found that the mechanical properties, while varying the individual layer thickness, yielded similar values as encountered in isotropically nanostructured nanocomposites.

In the present study the deformation mechanisms induced by indentation in nanomultilayered TiN/$SiN_x$ coatings were analyzed by TEM on lamellae cut by focused ion beam (FIB) through indents produced at different loads. We provide an experimental visualization of the damages caused to the coating during the different stages of

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deformation. It is shown which deformation processes happen at increasingly higher loads causing plastic deformation.

## 2. Experimental details

TiN/$SiN_x$ multilayered films were deposited by reactive unbalanced magnetron sputtering from elemental titanium and silicon targets. 100 repetitions of 5 nm TiN and 0.5 nm $SiN_x$ were prepared resulting in a total layer thickness of 550 nm. The operating pressure was 0.5 Pa at a sputter gas composition of Ar/$N_2$ of 4:1. The deposition temperature was kept at 200 °C; a negative substrate bias voltage of 70 V was used to provide for sufficient surface mobility of the growing film. For improved adhesion on the silicon substrates an interlayer of 50 nm TiN was applied. In order to enhance the interface smoothness at these low temperatures helium (amounting to 10% of the total gas flow) was added to the gas feed. The film quality in terms of single layer thickness and interface sharpness was verified by X-ray reflectometry. These results confirmed that the intended layer sequence and individual layer thickness was deposited. The TiN layers in the films have a pronounced [200] texture.

The TiN/$SiN_x$ films were indented at 100 nm, 250 nm, 500 nm and 1000 nm (initial penetration depth of the indenter tip) corresponding to 20%, 50%, 100% and 200% of the total film thickness by a Nanoindenter XP system with a Berkovich indenter tip in order to produce permanent deformation. The tip rounding was of the order of 50 nm. The indentation depths used in this study exceed by far those used for hardness determinations as it is intended to deliberately destroy the film in order to study the deformation mechanisms.

The microstructure of the as-deposited and indented TiN/$SiN_x$ multilayered films was studied by transmission electron microscopy in a conventional Philips CM30 equipped with a $LaB_6$ cathode and the high resolution transmission electron microscopy (HRTEM) images were obtained in a Philips CM300 with a field emission cathode both instruments operating at 300 keV. A focused ion beam instrument (FIB-Dual Beam FEI STRATA DB235) was used to prepare TEM lamellae through the indent in the multilayered coating as shown in Fig. 1(a). The obtained lamella with final dimensions of 20 μm × 5 μm × 80 nm, shown in Fig. 1(b) has the electron transparent area in its central part, and the indented film is clearly seen. It was transferred under an optical microscope onto a 3 mm Cu grid covered with a carbon film for TEM observations.

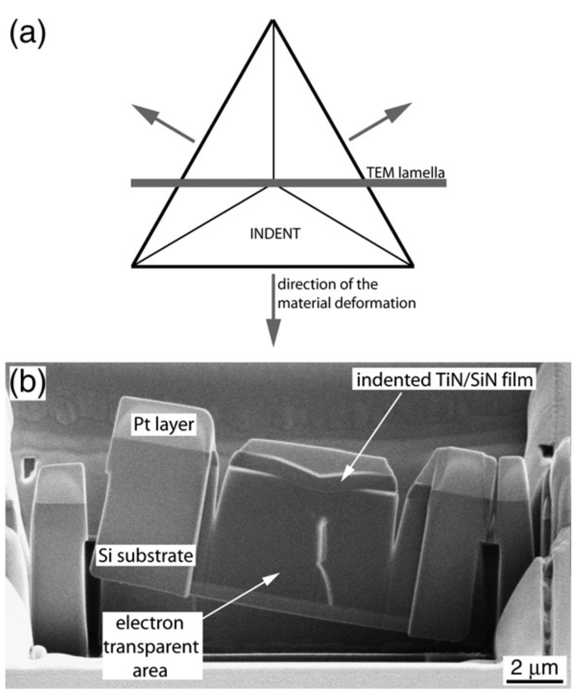


**Fig. 1.** (a) Schematic view of the lamella cut by FIB through the indent; (b) SEM image of the ready lamella cut through the indent: the delaminating coating and the crack in the substrate are clearly visible.

## 3. Results

Fig. 2(a) shows a dark field image taken with the (002) reflection of the TiN/$SiN_x$ multilayer sample composed of 100 repetitions of 5 nm TiN and 0.5 nm $SiN_x$ undeformed layers. The film is composed of crystalline TiN grains; the multilayering is evident, and it can be clearly seen that the $SiN_x$ layers inhibit the TiN crystallite growth to more than the intended 5 nm thickness or to form long columnar structures throughout the film thickness. Consequently it is assumed that no heteroepitactic relation is present between the TiN grains of adjacent layers. The selected area electron diffraction pattern inset in Fig. 2(a) contains strong reflections in the [200] direction, indicating texturing of the TiN, as already observed by X-ray diffraction (not shown here). Additionally, satellite reflections originating from the multilayering are visible in the central spot of the diffraction pattern.

The absence of heteroepitaxy across the $SiN_x$ layer is confirmed by the HRTEM image in Fig. 2(b) which shows differently oriented, equiaxed, crystalline nanograins with a diameter of 5 nm composing the TiN layers separated by regions having lighter contrast corresponding to amorphous 0.5 nm thick $SiN_x$ layers. The Fast Fourier Transform (FFT) patterns taken from different grains at positions 1 to 4 confirm the crystalline structure corresponding to the lattice spacing of *fcc*-TiN. Fig. 3(a) shows a TEM bright field image of a cross-section of the top part and the interface with the substrate of the TiN/$SiN_x$ coating indented to a depth of 100 nm. Directly under the indent apex a well-defined, triangularly shaped area is observed, in which the multilayering cannot be distinguished any longer as seen in Fig. 3(b). The Berkovich indenter tip angle is marked with the white dashed line. After tilting the sample by about 8° (see Fig. 3c), the multilayer structure is again visible and seems not to be altered: no compression of the layers was observed. The multilayers, which were visible in the intact region of the sample before titling, are then out of visibility under this angle, because these undeformed multilayers do not lie anymore in the observation direction. In the region of the indent onset several areas with seemingly double $SiN_x$ layers, marked by white arrows in Fig. 3(d), were observed and are discussed in detail further below.

Fig. 4(a) illustrates the cross-section through a 250 nm indent. The protective platinum top-coat was accidentally removed by the ion beam during the preparation of the TEM lamella by FIB and thus the area directly under the imprint is damaged by the $Ga^+$ ion beam. Nevertheless, the important features, such as open cracks in the lower part of the film shown in insets (b) and (c) in Fig. 4, and underneath these cracks some delamination from the substrate, indicated by white arrows in Fig. 4(a) are clearly visible.

The cross-section through the 500 nm deep indent is depicted in Fig. 5(a). In addition to the delamination of the film from the substrate, large, completely open lateral cracks at a depth of about one quarter of the film thickness from the substrate are observed. A median crack was generated below the indent tip as shown in Fig. 5(a). This crack does not run straight but follows the TiN grain boundaries as indicated by the white arrows in Fig. 5(b). Around this crack some bright lines are visible, which start from within the $SiN_x$ layers, seeming to penetrate the TiN crystallites or to double the $SiN_x$ layers. They are also found in the surroundings of the large lateral cracks at the bottom of the film, as shown by the white arrows in Fig. 5(c).

Fig. 6(a) shows a TEM bright field image of the cross-section through the TiN/$SiN_x$ film indented to a depth of 1000 nm with a median crack in the Si wafer appearing at the bottom of the image. Conversely to the 500 nm indent, the film indented at 1000 nm was