



ROBL-CRG

Experiment title:***In-situ* x-ray diffraction during reactive magnetron sputter deposition of Ti and Cu nanocomposites****Experiment number:****20_02_051****Beamline:****BM 20****Date of experiment:**from: 14.11.2001 to: 20.11.2001 (A) and
from: 24.04.2002 to: 30.04.2002 (B)**Date of report:**01.03.2002
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Report: (A)

In recent years, nanocrystalline materials have been introduced as a new class of materials with unique properties and a great potential for industrial applications. These properties are connected with the small grain sizes down to a few nm whereby an appreciable fraction of the atoms is residing in grain boundaries, i.e. atoms are situated in defect environments. This can result in high catalytic activity and high corrosion resistance and also in highly beneficial magnetic or mechanical properties. However, single-phase nanocrystalline materials are not stable with respect to thermal grain growth, which results in deterioration of their properties. To avoid this grain growth at elevated temperatures and to build additional beneficial properties into the materials, two-phase nanocrystalline materials, nanocomposites, can be introduced. E.g., the combination of a ductile phase (Cu) and a hard and brittle phase (ZrN) in a ZrN-Cu nanocomposite results in mechanical properties, that make the nanocomposite very suitable for a variety of tribological applications [1].

Nanocrystalline materials, including nanocomposites, are produced by many different techniques, e.g. melt spinning and vapour phase sputtering. Frequently, an intermediate amorphous phase is produced, which is transformed by thermal annealing into a two-phase amorphous/nanocrystalline material. In our experiment we wanted to ***study the nanostructure and its development during deposition of TiN-Cu composites by reactive magnetron sputtering***. This nanostructure depends on the deposition parameters, and such knowledge is required to tailor the nanostructure for optimum performance in specific applications. Before and after our experiments, we also did *ex-situ* x-ray diffraction measurements, additionally characterizing the phases appearing, the preferred orientation of the grains, the grain size and the microstrain as a function of the deposition temperature and the substrate bias voltage. ***At ROBL in-situ x-ray diffraction and reflection*** measurements were carried out, and, for various temperatures, the development of the nanostructure was followed as a function of film thickness, including in real-time. The nanostructure was also studied using a transmission electron microscope (***TEM***), while a scanning electron microscope (***SEM***) was used to measure the surface morphology. The film composition and thickness were obtained by Rutherford backscattering spectroscopy (***RBS***).

EXPERIMENTAL

The **deposition chamber** (together with the detailed **scattering geometry** and the quality of the data, like intensity, resolution, background, which can be obtained with the set-up) is described in detail in **Ref. 2**.

For the *in-situ* studies (incident x-rays monochromatized to 12.651 keV / $\lambda = 0.980 \text{ \AA}$), three different scattering geometries were used: (1) Bragg-Brentano large-angle scattering (XRD) revealing the texture, the out-of-plane lattice strain, grain sizes and microstrain (lattice defects). (2) Grazing incidence and grazing exit in-plane large-angle scattering (GIXS), with incident angle of 0.2° , i.e. a penetration depth of about 100 \AA , probing the crystallographic planes perpendicular to the surface. (3) Low-angle specular reflectivity giving film thickness and information on density and surface roughness.

Further experimental parameters were: base pressure $2 \times 10^{-5} \text{ Pa}$, target material $\text{Ti}_{80}\text{Cu}_{20}$ (element mixture of 99.999% pure Ti and 99.999% pure Cu, manufactured by induction melting on a water-cooled Cu crucible under a Zr gettered Ar-atmosphere), reactive sputter gas a mixture of Ar (99.9996%) and N_2 (99.99990%) with the ratio 4:1 at a total gas pressure of 0.6 Pa. The magnetron (only one at the time) was run at a dc power of 70 W, resulting in a **deposition rate of approximately 0.5 \AA/s** on Si(100) with a 180 nm amorphous oxide layer on top. The temperature varied from room temperature up to 700°C , a negative bias voltage of -30 V was applied.

RESULTS

At low-temperature depositions, due to a high N concentration, only a small amount of the fcc Cu phase was observed while for higher temperatures a strong Cu(111) peak developed (**Fig. 1**). The **texture changed with deposition temperature**, and the grain size increased (**no thermal grain growth**) and the microstrain decreased with increasing deposition temperature. Plotting the **microstrain** as a function of grain size, we found the data points to be lying on a single line similar to the **universal, empirical plots in the literature of microstrain versus grain size**. From the real-time measurements, it was found that **nanostructural changes only took place during growth**, not in between depositions, where the temperature was kept at the deposition temperature (**Fig. 2**). By SEM and cross-sectional TEM, **hillock-like protrusions at the surface** (TiN-Cu and pure Cu, as revealed by energy dispersive x-ray analysis) were observed at deposition temperatures above 300°C (**Fig. 3**) driven most likely by mechanical stress.

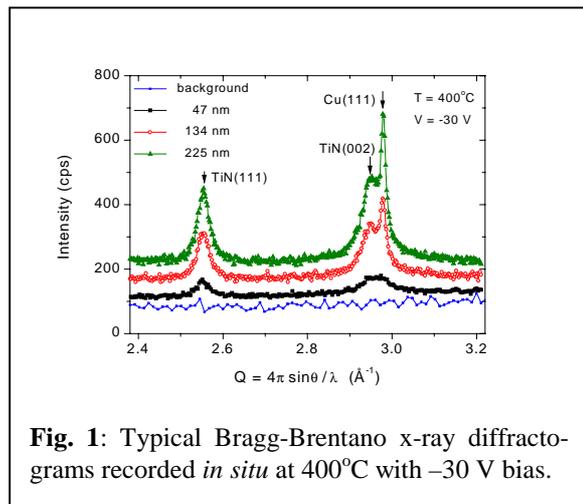


Fig. 1: Typical Bragg-Brentano x-ray diffractograms recorded *in situ* at 400°C with -30 V bias.

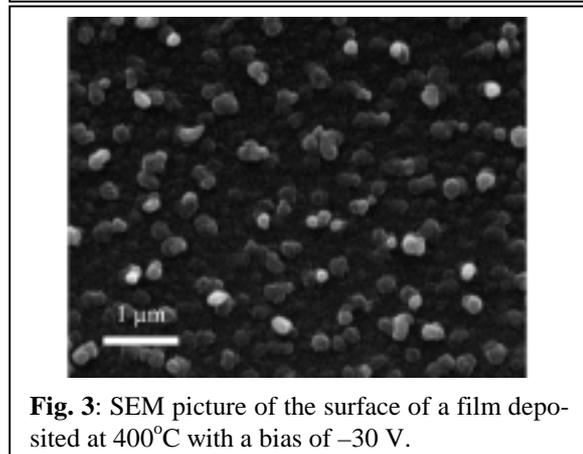


Fig. 3: SEM picture of the surface of a film deposited at 400°C with a bias of -30 V .

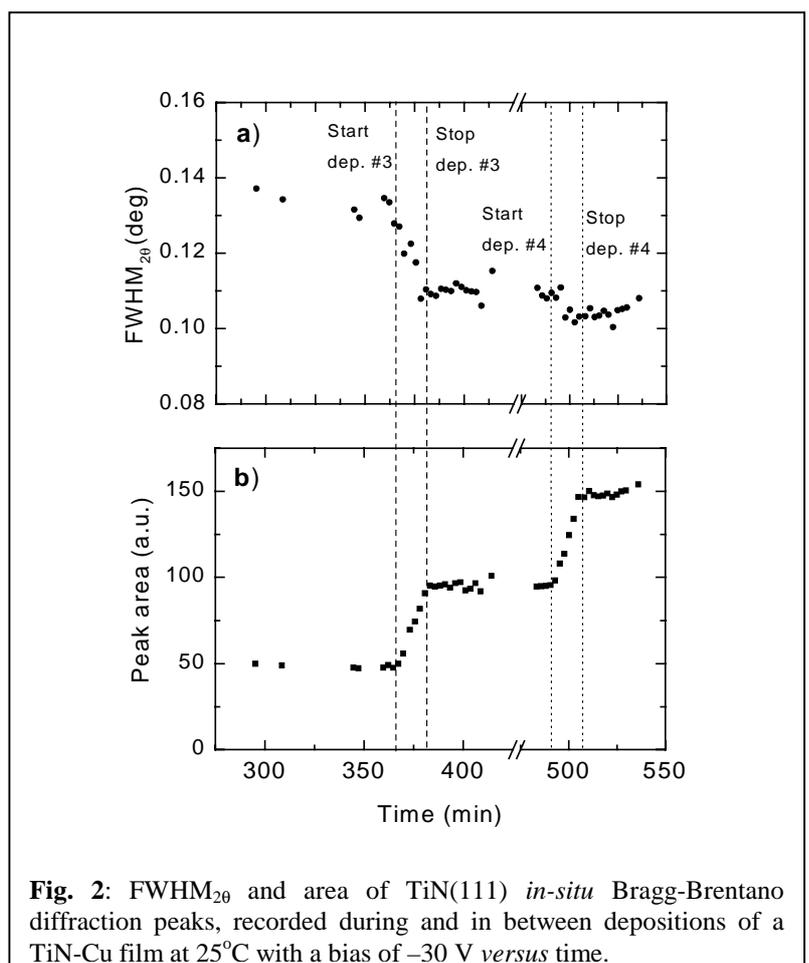


Fig. 2: $\text{FWHM}_{2\theta}$ and area of TiN(111) *in-situ* Bragg-Brentano diffraction peaks, recorded during and in between depositions of a TiN-Cu film at 25°C with a bias of -30 V versus time.

- [1] P. Zeman, R. Cerstvy, P.H. Mayrhofer, C. Mitterer, and J. Musil, *Mat. Sci. & Eng. A* **289**, 189 (2000).
 [2] W. Matz, N. Schell, W. Neumann, J. Böttiger, and J. Chevallier, *Rev. Sci. Instrum.* **72**, 3344 (2001).

