Texture Modification in Nano-crystalline Materials with Heavy Ions

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Introduction

Many properties of nano-crystalline materials differ from the properties of materials with larger grains. Among these grain-size dependent properties are the enhancement of specific heat, fast diffusion in nano-crystalline materials, the "inverse Hall-Petch" effect, and many others. The standard Hall-Petch effect describes the changes in elastic properties in polycrystalline materials. Plastic deformation in crystalline materials occurs through the pile- up of dislocations in the crystal. The high mechanical strength of fine-crystalline materials is also considered to be caused by the lack of dislocation source or a difficulty in dislocation multiplication in small grains. However, some nano-crystalline materials (grain size 5-100 nm) obey the inverse Hall-Petch rule, showing the softening when the grains get too small. Since the grains are still too small to allow a pile-up of dislocations, deformation in these materials must be described by another process. The most promising candidate is the process which includes sliding of the grains along the grain boundaries. In a series of ion irradiation experiments we managed to activate the grain sliding even in materials with grains larger than 30 nm. Taking advantage of the nature of the interaction between swift heavy ions and solids we introduced thermal energy directly in grain boundaries, resulting in grain rotation and sliding, which was later verified by measuring the texture of thin layers at the KMC2 beamline at BESSY synchrotron light source. First indications for grain movements were seen by fortune in Munich during heavy ion sputtering experiments with 200 - 275 MeV Au ions some years ago [1].

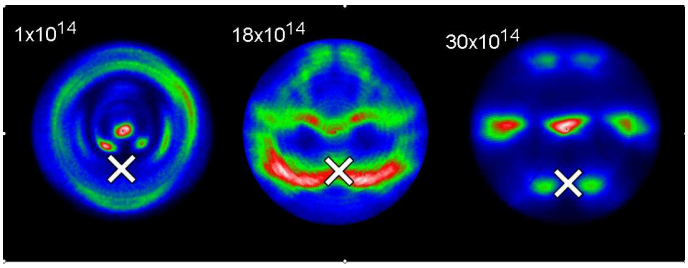

Fig. 1: Combined pole figures of 110 and 101 planes in the nano-crystalline Ti layer in gray scale after irradiation with different fluences (black for low intensity, white for high intensity). Fluences in ions/cm^2 are indicated in the corresponding pole figure. White 'x' marks the direction of the incident beam. Concentric rings originating from cylindrical symmetry are very pronounced after a fluence of 1x10^{14} ions/cm^2. In the second pole figure, after 18x10^{14} ions/cm^2, the texture rotated about 60° upwards. Although the rings are still observable, the braking of the cylindrical symmetry has already started. After 3x10^{15} ions/cm^2 the texture rotation stopped and a mosaic texture showing the symmetry of the hexagonal lattice is visible. 100-lattice plane is now parallel to the surface.

Experiments

Polycrystalline Ti, Pd, and TiN layers were irradiated with 350 MeV Au ions with different fluences up to 3x10^{15} ions/cm^2. The incidence angle of the ion beam was chosen to be different from normal incidence to the sample surface to be able to separate the influence of the sample surface and the ion beam. Irradiation was performed at the ISL heavy ion accelerator at Hahn-Meitner-Institute in Berlin. Irradiation of samples with swift heavy ions is a time consuming task. For this reason we performed stepwise irradiation to accumulate a high fluence and texture characterization of the samples between subsequent irradiations. Textures were measured at the diffractometer experimental station at the KMC2 bending magnet beamline at BESSY using photon energy of 8 keV. A combination of an area-sensitive wire detector and intense synchrotron beam allowed very fast acquisition of a complete orientation distribution in the sample (see BESSY Annual Reports 2003/4). Additionally, the area detector allowed simultaneously the determination of the grain size. However, since the grains grow during the irradiation, the resolution of the area detector is sufficient to estimate the grain size only at the beginning of the irradiation and a possible trend has to be estimated.

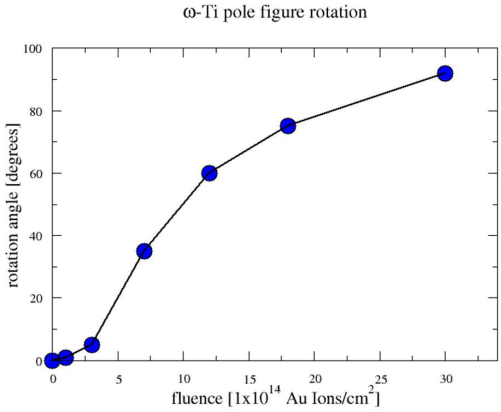

Fig. 2: Dependence of the angle of the grain rotation on the fluence. Beyond 1x10^{15} ions/cm^2 starts slowing down of the rotation

Results

We measured the change of the crystalline orientation distribution after the irradiation with swift heavy ions. The further irradiation of already studied samples up to a fluence of 3×10^{15} ions/cm^2 revealed some interesting and new effects. In different nano-crystalline materials we observed two distinct changes with different magnitude:

i) the texture rotated continuously away from the incidence direction of the ion beam. New is that this rotation slows down and stops when the 100-lattice plane becomes parallel to the surface.

ii) the cylindrically symmetric texture, specific for the deposited films, broke into a mosaic texture improving the alignment between the grains. At the beginning of the irradiation the grain size was estimated to be around 50 nm. Already at fluences of 1.8×10^{15} ions/cm^2 grains were larger than 100 nm and could not be resolved in this experiment anymore.

Discussion

Since the texture in highly irradiated samples rotated by almost 90°, we can not explain the rotation through the interaction of the ion beam with the crystalline grains in the sample. However, the grain boundary, which is supposed to be amorphous, is in polycrystalline materials few nanometers thick. If the grains are of the size of 10-100 nm, large part of material is located in the grain boundaries, i.e. amorphous. There is a well-known effect, referred as "ion hammering", which describes anisotropic elongation of amorphous materials during ion irradiation [3]. Swift heavy ions deposit their energy in solids mainly through electronic interaction. Since the collisions with solid nuclei are unlikely at high energies, ions travel through the solid on an almost straight path. The energy deposition is concentrated in a cylinder few nanometer around the ion track. Due to the cylindrical shape of this volume, the material is plastically lengthened in the direction normal to the ion path and shortened in the direction parallel to it. If the amorphous layer fixed on the substrate is bombarded with swift heavy ions from a direction other than normal, elongation is transformed into shearing of the layer away from the direction of incoming ion beam. This effect is not observed in crystalline samples.

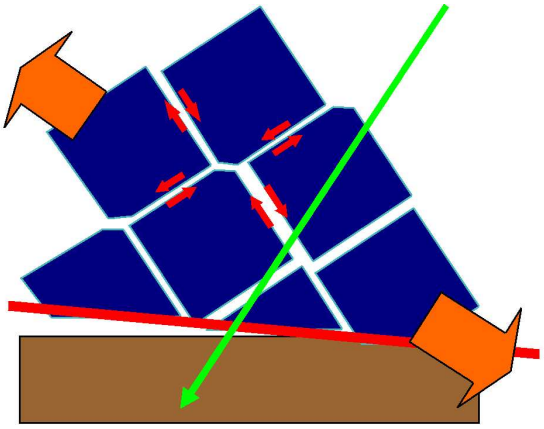

Fig. 3: Shearing of the nanocrystalline layer schematically shown as the sum of the grain boundary shearing. Long arrow marks the direction of the impinging ion beam. Grain boundaries, behaving like thin amorphous layers are sheared in the direction of small arrows. As the grains are sliding along the boundaries, net elongation of the layer is resulting in the direction normal to the ion beam (fat arrows). This dilatation tends to tilt the bottom interface of the layer. However, since the layer is fixed on the substrate, similar like in amorphous layers, the indicated line must stay horizontal resulting in the rotation of the whole layer together with the grains within. In our texture measurements we observe this rotation.

To measure the shearing of the nano-crystalline layer, a gold marker was deposited on the surface of the sample. The translation of the marker was measured in-situ during the irradiation. A comparison with a mean-field calculation for the shearing in amorphous Ti layer (it is not possible to grow an amorphous Ti layer) showed that the measured nano-crystalline Ti layer shears with 2% of the expected rate for homogeneously amorphous Ti. This indicates that there is 2% amorphous material in the nano-crystalline Ti, which corresponds to the volume contained in 0.5 nm thick grain boundaries for 60 nm large grains. This would also, in connection with the measured grain growth, explain the slowing down of rotation due to the grain growth. However, the mean-filed theory and shearing measurements fail to explain the breaking of the cylindrical symmetry in textures. The change of the symmetry can only be explained by the rotation of grains with respect to their neighboring grains, which implies a sliding of the grains along boundaries or more complicated creep processes. Grains rotate until they reach a minimum in grain boundary energy, i.e. the grain boundary matches a low-indexed crystalline plane. It is obvious that the sample does not behave like a partially amorphous layer. The grain boundaries themselves rather behave like individual thin amorphous layers. Thus, the shearing occurs between two grains applying a rotational momentum on individual grains as illustrated in Fig. 3.

References

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