Deformation Under Nano/Microindentation of LiF, MgO, Si Monocrystals Stipulated as Support Materials for Cu/substrate Structures

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***Abstract* — This work is focused on the specific behaviour of LiF, MgO, Si single crystals when they are put to test by the local nano and micro loading, because they are stipulated as support materials in Cu/substrate structures. These crystals belong to cubic syngony with ionic, ionic-covalent and covalent chemical bond type, respectively, and are possessed of very different dislocation mobility. It is expected that these factors will very hard influence on the mechanical properties of the Cu/substrate composite structures. That is way, the microhardness and specific deformation zones around nano and microindentations created under concentration load action are considered in the paper. It is shown that these monocrystals essentially differ from each other in the hardness and form various relief and dislocation rosettes around indentations.**

I. INTRODUCTION

Behaviour of composite structures (CSs) of the type "soft submicron film/hard crystal substrate" under external local loading is too little studied today. Especially, there is no enough information about the mechanical properties of such a structure 'as an entity', and about the deformation process evolution on the dislocation level in substrate, which is main component of composite structure (CS). At the same time, such structures are largely used in modern nanotechnology, and understanding of these problems is very important. The problem of study of mechanical properties of the „thin film/substrate" CSs and its response peculiarities in dependence on the loading value under dynamical nano/microindentation put some questions before researchers about the reciprocal influence of film and substrate.

In some works [1-4], it is shown that mechanical properties of CSs, consisted of a thin nano- or microscopical film deposited on the bulk substrate, depend on many factors, and one of the main among them is the substrate mechanical ones. Therefore, it is of interest to consider the regularity of creation of the deformed zone in the indentation neighbourhood on the surface and in the bulk of crystal-substrates.

It is known, that copper (Cu) has a face-centered cubic lattice. So, for the Cu/substrate CS study it is of interest to use, as substrate materials, the crystals which belong to the same system, as well. That is why, the Cu/LiF, Cu/MgO, Cu/Si CSs were selected for work. The LiF, MgO and Si crystals belong to the cubic syngony, but they have the different type of bond: ionic (LiF), ionic-covalent (MgO), and covalent (Si). Because of different type of chemical bond, these crystals strongly differ from each other in the microhardness values and the individual dislocation velocity. The LiF microhardness value is close to Cu one (H_{Cu} =1.0 GPa; H_{LiF}=1.2 GPa). As opposed to the LiF crystals, MgO and Si ones have the hardness much more than Cu: H=8.0 GPa and 9.5 GPa for MgO and Si, respectively. On the other hand, the LiF and MgO crystals possess a high dislocation velocity (v_{LiF}= 10^{-5}-10^{0} cm/s; v_{MgO}= 10^{-6}-10^{-2} cm/s), at that time a very low velocity is characteristic for the Si crystals (v_{Si}= 10^{-7}-10^{-4} cm/s) [5,6]. Due to this fact, at room temperature in LiF and MgO crystals, the developed dislocation rosettes are formed in the indentation neighbourhood, which can be revealed by a selective chemical etching even at the very low loading (*P*=10-20 m*N*). Whereas in the Si crystals, the dislocation rosettes of indentations made at the room temperature, create a dense submicron zone close to the indentation, which can be visualized only by using the transmission electron microscopy. Taking into account similarity and difference of the crystallography, of the strength and plastic parameters of these crystals, one can with good reason expect a peculiar contribution of substrate to creation of the Cu/substrate CS and its response, as an united material, to the external load action.

Therefore, in this work the objective to analyse the specific deformation of these crystals under indentation in order to compare later on the behaviour of 'pure' crystals (without films) with the same of the Cu/LiF, Cu/MgO, Cu/Si CSs obtained by two methods: thermal spraying, and magnetron sputtering. This analysis will allow at early stage to reveal the deformation in substrate under indentations made on the Cu film and step-by-step to follow its evolution under loading increase.

II. RESULTS

Micro and nanoindentation methods were used to study the specific deformation of the LiF, MgO, Si single crystals on plane (001). The quasistatic indentation was carried out using the PMT-3 microhardness tester equipped by the Vickers and Berkovich diamond pyramids. The dynamical indentation using the Berkovich diamond pyramid was made on the PMT-3-NI-02 nanotester. The loads varied within the limits of P=10-1000 mN. The deformed zones near the indentations were studied by the atomic force (AFM) and scanning electron (SEM) microscopy together with the selective chemical

etching. The next compositions of etching solutions for the dislocation detection were used: a diluted water solution of $FeCl_3$ – for LiF, the water solution of NH_4Cl (5 p.) + H_2SO_4 (1 p.)] – for MgO, and $K_2Cr_2O_7$ (2 p.)+ H_2O (10 p.) + HF (2 p.) solution - for Si.

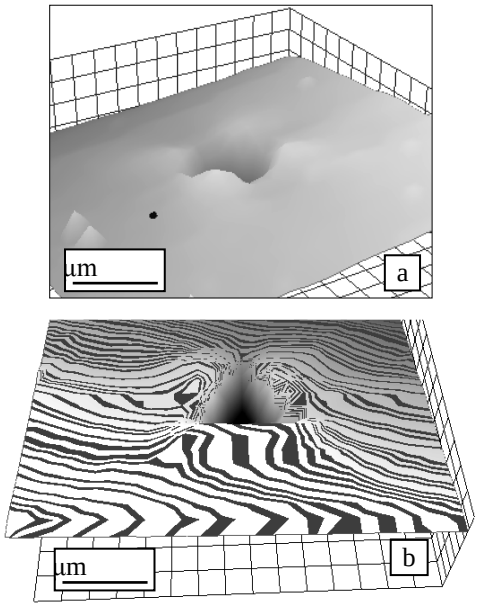


Figure 1. AFM. The plane (001) of LiF crystal. The 3D images of indentations made by Vickers (a) and Berkovich (b) indenters with P=10mN. Computer rendering of plastic fragmentation caused by indentation (b).

As far as, it is planed to study the morphology around indentations on Cu/substrate CSs in the interval of nano and micro loads, it was necessary to follow the evolution of substrate crystals in the same load interval. It is known [7], that pile-ups (hillocks) of displaced (forced-out) materials appear along <110> direction near the imprints when the microindentation by Vickers pyramid is made on the (001) plane of ionic and ionic-covalent crystals.

The AFM shape of the Vickers (a) and Berkovich (b) nanoindentations (P=10 mN) is shown in the Fig. 1. The computer rendering of AFM images (Fig. 1 b) gives an opportunity more clearly to visualize the surface relief around indentation. One can see, the relief with the maximal forced-out material along <110> is formed under even very delicate load, that is determined by the specific of load application, by crystallography and sliding elements of crystals [7]. At the same time, the form and orientation of indenter make changes in the pile-up position of displaced materials. The maximal pile-ups near the Vickers indentation are symmetrically situated along <110> direction (Fig.1a), but near the Berkovich indentation, with ternary symmetry, the relief has an asymmetrical shape – two pile-ups are oriented along <110> directions and two ones unite with each other and create a common wall in the line of <110>-<100>-<110> directions. At the load increase, the image qualitatively maintains, but dimension of pile-ups essentially increases. It is bound with growth of the quantity of material forced-out from under the indenter (Fig.2).

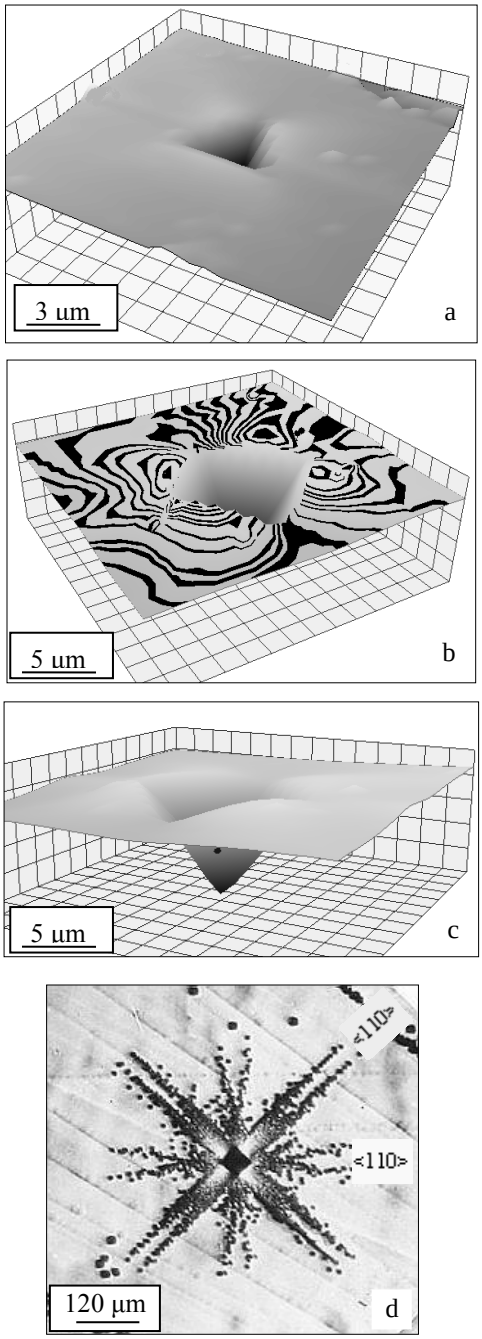


Figure 2. AFM, the LiF crystal, plane (001). The 3D images of indentations made by Berkovich (a) and Vickers (b,c) indenters. The dislocation rosette around the indentation made by Vickers indenter (d). P, mN: 12 (a), 200 (b,c), 1000 (d).

Nevertheless, a special feature was observed. Due to high dislocation mobility, the forced-out material no results in the significant growth of the hillock height under load increase and enlarges the pile-up area, as 'spreading' on the surface. It is obvious if compare the Fig. 1 a,b with Fig. 2 b,c. Under the low loads (10 mN), the pile-ups comes close to the indentation, but under P=200 mN the forced-out materials is distributed on the area 4-5 times more than indentation one (Fig. 2 b,c). This result correlates with the shape of dislocation rosette

revealed by the selective chemical etching (Fig. 2 d). One can see, that the dense dislocation zone (regions of white colour), along the <110> direction, is one and a half time more than indentation side (*a*), but the length of dislocation arms (*L*) is 6-7 times more than (*a*).

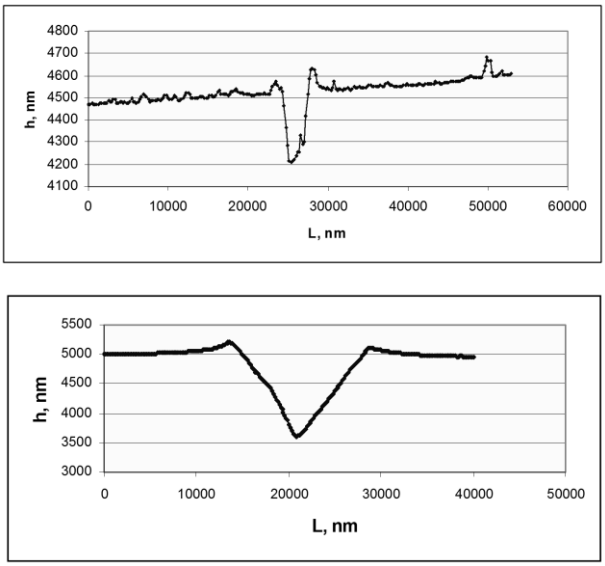


Figure 3. The cross-sectional profiles of indentations made by Berkovich indenter on the MgO crystal. P, mN: 120 (a), 1000 (b).

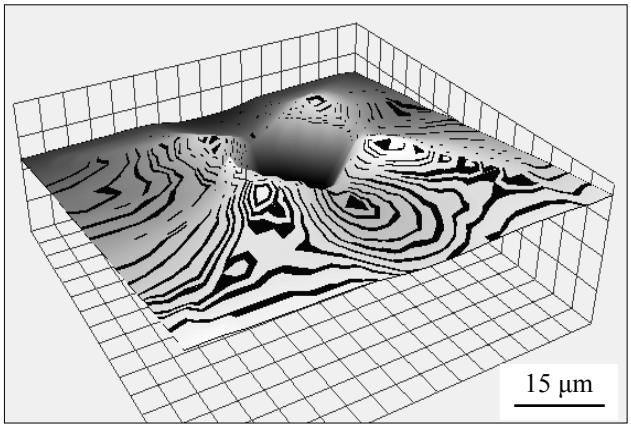


Figure 4. AFM, the MgO crystal, plane (001), P=1000mN. A computer rendering of equal high level lines on the pile-ups in the indentation neighbourhood where the contours of many facets can be distinguished.

So, the surface area, on which the pile-ups are expanded (S_p), constitute $S_p \approx (4\text{-}5)S_i$, here S_i is the area of indentation projection, whereas a total area of the defect zone (the dislocation zone) in the indentation neighbourhood (S_{dz}) is 125 times more than indentation projection area, $S_{dz} \approx 125S_i$. Such a defect zone creates in the crystal bulk the elasto-plastic tensions which lead to internal stresses in the Cu/substrate CS. The internal stresses can bring to decrease of adhesion force between film and substrate and even to the film delamination in the indentation neighbourhood. The similar regularity was noted for the MgO crystals, as well (Figs. 3-5).

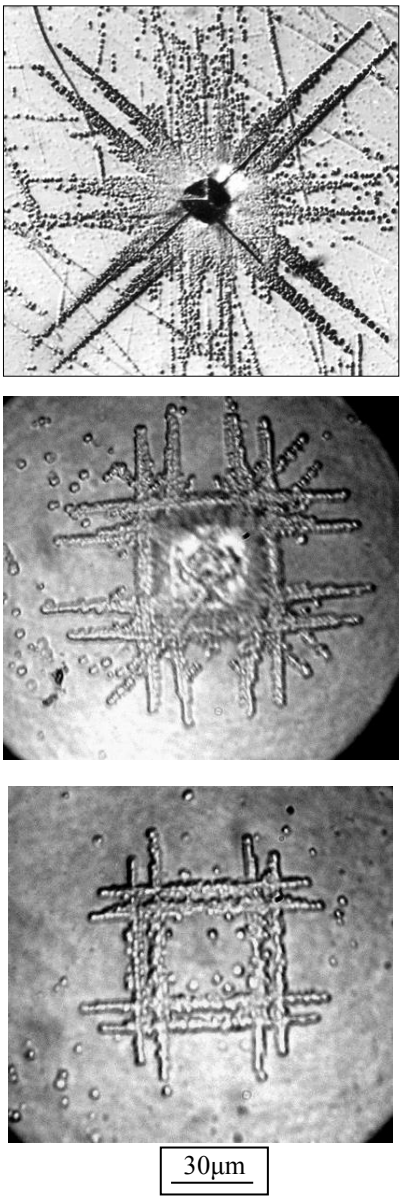


Figure 5. Light microscopy (LM), the MgO crystal, plane (001), P=1000 mN. The evolution of the dislocation zone in the indentation neighbourhood in process of the sequential polishing/selective etching of the indentation.

At the same time, the different velocity of individual dislocations introduced some modifications in the dimension and arrangement of pile-ups. They became higher and situated near by the indentations on the MgO crystals (Fig. 3, 4). In addition, as it follows from Fig. 5, the dislocation density in arms is very high, and the central part of the dislocation rosette, which approximately corresponds to the dimension of zone encircling the pile-ups, takes up an area $S_p \approx 5S_i$, whereas the dimension of the whole defective (dislocation) structure is $S_{dz} \approx 100S_i$. So, one can see, the material, forced-out from under indentation, occupies far larger area, than in the LiF, however area of dislocation zone is less: $S_{dz\ MgO} < S_{dz\ LiF}$. This result, in our opinion, may be caused by several reasons: (i) by lower velocity of the individual dislocations in the MgO crystals as compared with the LiF ones (see above); (ii) as a result of it, by

creation of more dense and complicated dislocation structure in the indentation neighbourhood; (iii) by a heightened brittleness of the MgO crystals (Fig. 5 a,b), as a result of accumulation of too high internal stresses in the indentation region, generated by huge aggregation of dislocations.

As was shown above, the velocity of individual dislocations in silicon is essentially less than in LiF and MgO. This fact, no doubt, will affect the character of formation of the surface relief near the indentation and the development of dislocation structure around it. The indentation shape and relief around it in two 3-D projections are shown in Fig. 6. The indentation is made by Vickers indenter with the 90 mN load.

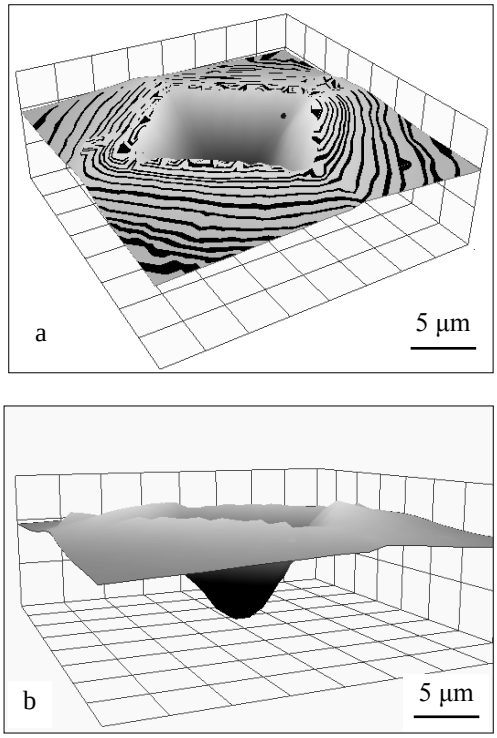
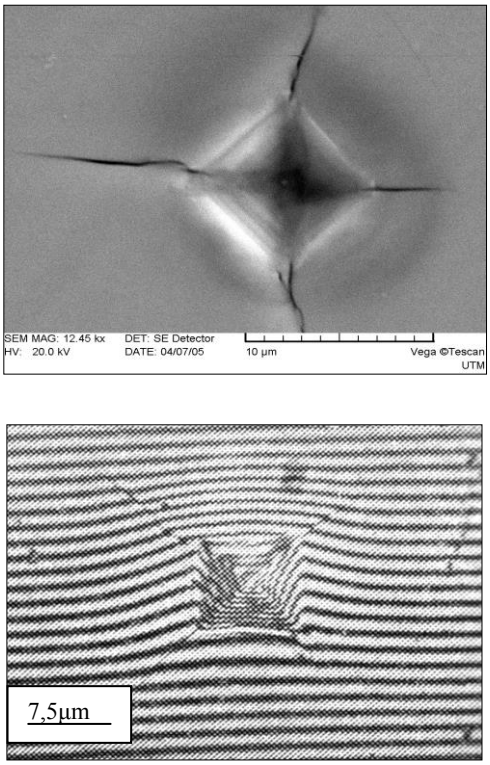


Figure 6. AFM. The Si crystal, plane (001). The 3D images of indentation made by Berkovich indenter and shown in two projections. P=90 mN. A computer rendering of equal high level lines on the pile-ups in the indentation neighbourhood where the contours of many facets can be distinguished (a).

One can see, the displaced material is situated rather uniformly around indentation, without any predominant direction, how it was revealed for the LiF and MgO crystals. Microfragmentation of surface structure in form of facets occurred in immediate proximity to the indentation [8]. In the regime of computer rendering, the microfragmentation is very clearly visible in form of triangular and trapezoidal figures directly on the indentation margins (Fig. 6 a). In other projection, the facets can be seen as a toothed bordering of the indentation edge (Fig. 6 b).

It is known [9-11], a phase transition takes place in Si under indentation. Monocrystalline silicon turns into some other phases. The principal of them are: Si-II, metallic phase, which appear under indenter during its penetration in crystal. This phase is an unstable one and changes into Si-III, Si-XII phases and amorphous silicon (a-Si) [9-11]. A thin dislocation interlayer with the micro-level thickness (1-2μm) appears between zone, occupied by the new phases under indentation, and the bottom monocrystalline structure of Si [12]. Because of very thin dimension of this dislocation zone, it cannot be visualized using the selective chemical etching, as it was obtained for the LiF and MgO crystals. This zone can be detected only by the method of transmission electron microscopy [13, 14].



b

Figure 7. The Si crystal, plane (001). The shape of indentation in regime of the second electrons in the SEM (a) and an optical interference pattern in its neighbourhood (b). P=500 mN.

An important conclusion follows from this result: the appearance and size of the pile-ups on the surface around indentation on silicon does not coincide with dimension of the dislocation zone. Really, the area, occupied by the pile-ups and uniformly distributed around indentation, approximately is 5 times more than indentation area ($S_p \approx 5S_i$), while the dislocation zone near the indentation has a micron-level dimension, i.e. $S_{dz.} \approx S_i$. One of the causes for this phenomenon, it seems to be the occurrence of new phases, which have the smaller density, than the monocrystalline silicon and ought to take up a lot of volume around indentation [9,13]. Another reason of the above mentioned phenomenon can be appearance of the brittle destruction in the form of thin cracks, as extension of the indentation diagonals, delaminations or chippings off at high loadings (Fig. 7, 8). We found that short cracks appeared under the 100-200 mN loadings, already.

Note, that the following result attracts our attention. Regardless of the physical nature of the pile-up origin (dislocation or phase transfer) the ratio $S_{p.}/S_i$ is about 5 for all studied crystals. It indicates that appearance of the

pile-ups is determined by other reason, namely, by the stressed state created in crystals under concentrated load action.

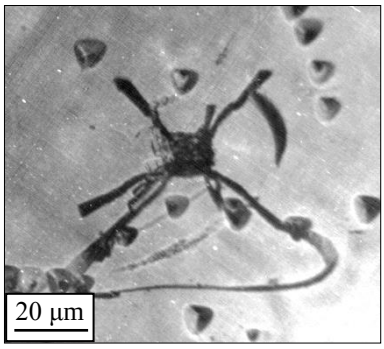


Figure 8. LM. The surface morphology of the deformed zone near indentation made on the (001) plane of the Si crystal. P= 1000 mN.

Using the respective equation from the theory of plasticity [15], it was estimated the relation between the indentation diameter (*d*) and dimension of the region covered by plastic shear (*D*). It was shown that $D \approx 2.1d$. This implies that $S_D \approx 4.4 S_d$, which is approximately equal to the ratio $S_p/S_i \approx 5$, characteristic to crystals studied in the work.

Thus, the obtained results show that the surface relief around indentations detected on the crystals, even belonging to the same crystal system, can be of different nature. It can provoke the various modifications of lattice parameters and, in so doing, to create unequal internal stresses in the indentation neighbourhood. These factors, undoubtedly, will influence on the mechanical parameters of the fabricated 'film/substrate' CS, particularly, of the Cu/substrate composite structures.

III. CONCLUSION

The obtained results have shown that a large range of the velocity and mobility of dislocations in the studied substrate-crystals is an undoubted factor which can affect the specific of deformation and mechanical properties of the Cu/substrate structures, fabricated on its base.

In addition, the alteration of the film thickness for the same substrate, in turn, can influence on the image of deformed zone around indentations, because the substrate effect is inversely proportional to film thickness. The more is film thickness, the less is substrate influence for the same loading value.

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