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Thin films of blue bronze – production and characterization

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Here, we present results of collaboration between various groups from several countries in order to prepare and characterize thin films of charge density wave (CDW) system $K_{0.3}MoO_3$ suitable for time-resolved THz conductivity measurements.

In preparation of $K_{0.3}MoO_3$ thin films we have followed the early approach by Van Zant and colleagues, who have already succeeded in preparing films of good quality [1-5] of very similar compound $Rb_{0.3}MoO_3$. We have used pulsed laser deposition (PLD) for the growth of $K_{0.3}MoO_3$ thin films. All depositions were performed onto both (510) $SrTiO_3$ (STO) and (1-102) Al_2O_3 (ALO-sapphire) substrates. The target material was prepared by grinding single crystalline samples and pressing them into pallets. Both targets and substrates were placed into a vacuum chamber where oxygen pressure was suitably controlled. A pulsed KrF excimer laser (model COMPexPro 205 from Lambda Physics Coherent) was used to create plasma plume by ablating material of a rotating polycrystalline target. The particles contained within the plasma plume are deposited on the substrate which is mounted on a heater block opposite to the target. The stoichiometry and morphology of the deposited film strongly depends on the thermodynamic conditions during the film growth. The most important parameters include the substrate temperature, the oxygen pressure in the chamber and the deposition rate. $K_{0.3}MoO_3$ films can only be grown in a narrow range of growth parameters [6].

In the following we describe the results of various characterization methods used to determine sample stoichiometry, morphology, transport and optical properties. Figure 1. shows raw results of TOF-ERDA experiment executed by iodine beam on BB14 film on ALO substrate.

Grazing incidence X-ray diffraction (GIXRD) measurements were carried out with a modified SAXS experimental setup [6], adapted with tilting specimen stage for grazing incidence. The GIXRD curve(s) were acquired with position sensitive detector (Hecus PSD-50M) in the 2θ range between 8-13 degrees.

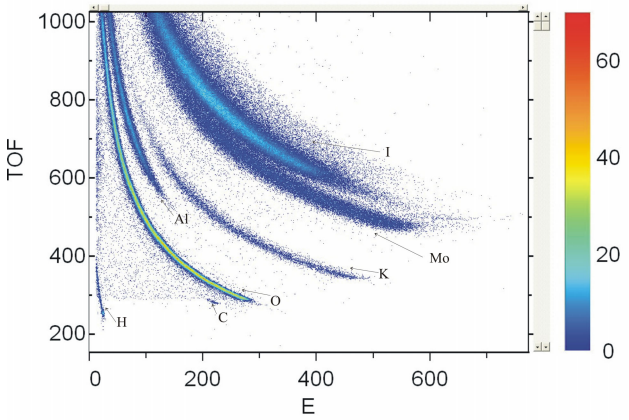

Figure 1. Traces of hydrogen and carbon are detected from the film surface, while potassium, molybdenum and oxygen atoms are determined to form 320 nm thick film in stoichiometric ratio K:Mo:O = 0.25:1:4 in average. Aluminum and oxygen from substrate are also detected.

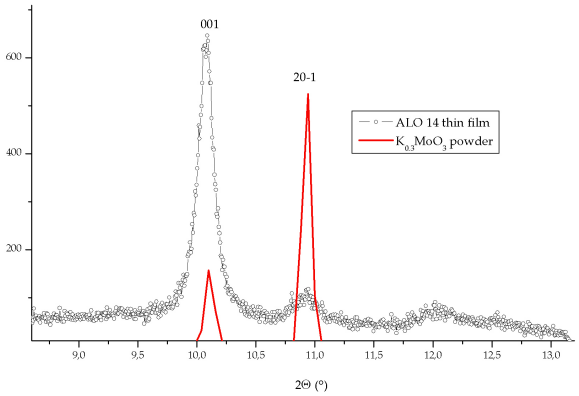

Figure 2. GIXRD spectrum of a $K_{0.3}MoO_3$ film BB14 grown on an ALO substrate (dots). As a comparison, on the same graph is plotted the calculated XRD spectrum for powder $K_{0.3}MoO_3$ (red line). X-ray wavelength is 1.54 Å.

Figure 2. represents GIXRD spectrum of a $K_{0.3}MoO_3$ film grown on an ALO substrate (dots). The measured pattern was compared with crystallographic data from data bank for monoclinic $K_{0.3}MoO_3$ powder phase [7] (red). Although small region in 2θ space is explored, two Bragg peaks, designated as (001) and (20-1), can be attributed to the K-BB phase. Furthermore, their intensity ratio in this thin film indicates that K-BB grains are textured with preferred (001) orientation parallel with surface.

In the second stage of characterization, the films were further analyzed using the atomic force microscopy (AFM) measurements (Figure 3.) performed with a commercially available atomic force microscope (Nanoscope Dimension DI3100 with Nanoscope IV controller from Veeco Instruments).

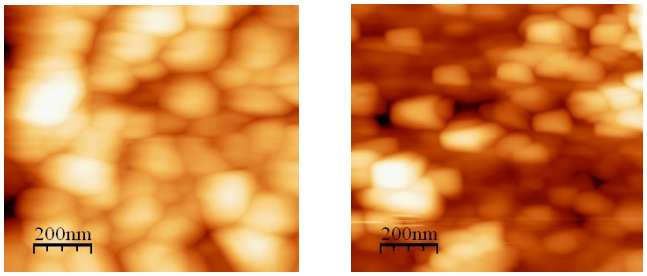

Figure 3. a) BB13 film on ALO substrate average roughness is 45 nm, with grain sizes up to 200 nm b) BB13 film on STO substrate average roughness is 33 nm, grain sizes are 150- 200 nm, with several larger grains around 350 nm.

Four contact resistivity measurements were performed in bulk and on film grown on sapphire substrate in temperature range 100 K-300 K, as shown in inset of Figure 4.. Peierls transition to CDW state in the bulk can be seen as a narrow peak in derivation of logarithm of resistivity in respect to inverse of temperature (Δ) at transition temperature T_P, followed by constant value of Δ (around 450 K) below T_P and metallic state above T_P, as seen in Fig. 4. and in inset.

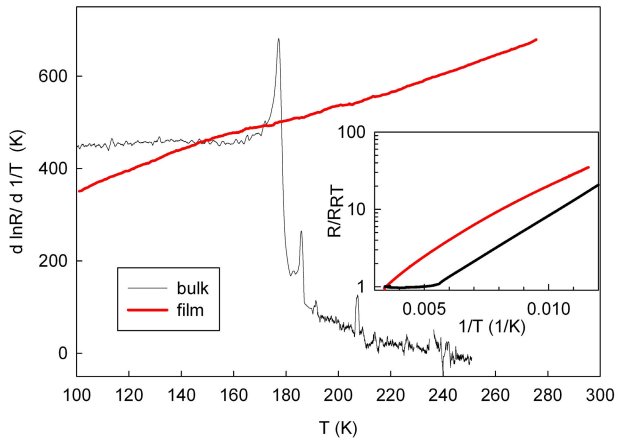

Figure 4. Transport measurements on $K_{0.3}MoO_3$ bulk and on $K_{0.3}MoO_3$ film on Al_2O_3 substrate are compared.

While in the bulk transition to CDW state occurs at 177 K, none of the three features mentioned are present in the film. Instead, almost linear Δ-T dependence with a slight change of slope at around 150 K is observed. Authors suggest that the reason for this are disjoint grains and/or grain boundaries in film that are hiding both the metallic feature and semiconductor feature (constant Δ), along with size effects that are smearing the transition and lowering T_P.

We studied both temperature and excitation density dependence of photoinduced (PI) reflectivity changes using an optical pump-probe technique. The induced changes in reflectivity (R) were recorded utilizing a fast-scan technique, enabling high signal-to-noise levels [8]. Figure 5. represents temperature dependence of the PI reflectivity change as a function of temperature and time after photoexcitation. The recorded ΔR/R traces on thin films are qualitatively similar to those recorded on single crystals, however a) the amplitude of the induced change was substantially lower than in crystals despite the fact that films are optically thick and b) the damping of the coherently excited phonon modes is also substantially stronger than in the case of single crystals.

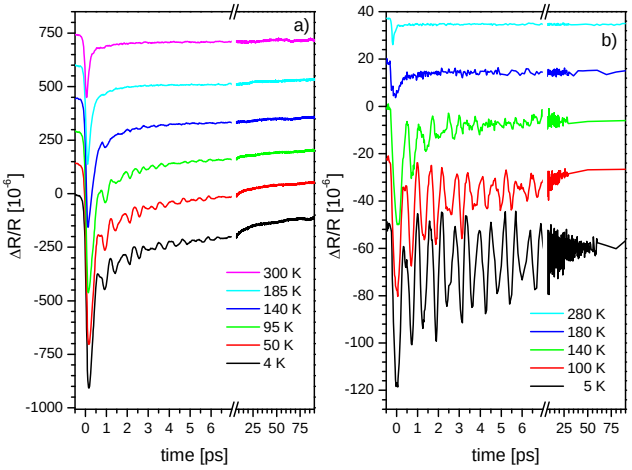

Figure 5. a) PI reflectivity dynamics in K0.3MoO3 film on Al2O3 substrate as a function of temperature. b) PI reflectivity changes in bulk K0.3MoO3 as a function of temperature.

It is clear from the measurements on thin films that we have manufactured a series of thin films of $K_{0.3}MoO_3$. Femtosecond pump-probe spectroscopy has proven to be the most reliable characterization tool in determining the presence of the CDW formation in films. Judging by the dynamics, one could conclude that there is no drastic difference between the physics of $K_{0.3}MoO_3$ in bulk or in films. The main difference between the bulk and thin films was one order of magnitude smaller amplitude of the PI electronic signal together with smaller amplitude and stronger damping of all phonons. This can be attributed to two different phases of the material. The domain sizes are so far unknown so a future study, where the data on films would be compared to a series of systematically irradiated $K_{0.3}MoO_3$ crystals could shed more light on this problem. This is because irradiation introduces impurities in the crystal so domain size can be systematically decreased.

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