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Influence of deposition parameters on pulsed laser deposition of $K_{0.3}MoO_3$ thin films

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Abstract: Pulsed laser deposition (PLD) has become the most important technique for the production of new materials with complex stoichiometry and multilayered structures. In this paper we present parameters that influence the production of $K_{0.3}MoO_3$ (KBB) thin films by PLD. KBB is a quasi-one-dimensional (q-1D) conductor that exhibits transition to a new ground state of charge density wave (CDW) below a transition temperature *Tp*. It is considered to be a “canonical“ CDW system and its properties have been extensively researched in bulk. In recent years, production of KBB thin films has enabled investigation of CDW properties in the conditions of reduced dimensionality. Choice of deposition parameters highly influences production of the films and therefore it is essential to investigate it in order to obtain high quality films. This investigation enables one to determine optimal conditions for the production of KBB thin films by PLD.

INTRODUCTION

Metals with a chain-like structure which are highly anisotropic and therefore can be considered as quasi-one-dimensional (q-1D) exhibit a transition to a new ground state of charge density wave (CDW). Potassium blue bronze (KBB) is a commonly researched inorganic system with CDW, but it has not been produced in thin film form until recently (Starešinić et al., 2012; Dominko et al., 2011; Đekić et al., 2015; Đekić et al., 2013). It has a deep blue color hence the name “potassium blue bronze”. Our main motivation for KBB thin films production was the investigation of reduced dimensionality effects on CDW properties of the material (Borodin, 1986; Zaitsev-Zotov et al., 1992; Zaitsev-Zotov et al., 2010; Schneemeyer et al., 1984; McCarten, et al., 1992).

Properties of the obtained films depend on production parameters such as: ambient gas and pressure, substrate temperature, incident laser fluence, deposition geometry and repetition rate. Deposited films were characterized using several standard characterization techniques: ultraviolet-visible (UV-vis) spectroscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM), time-of-flight elastic recoil detection (TOF-ERDA), electrical transport measurements and femtosecond time-resolved spectroscopy (fs-TRS). Investigation of the influence of deposition conditions on the quality of the films enabled us to determine optimal conditions for further depositions.

EXPERIMENTAL PROCEDURE

In pulsed laser deposition (PLD) technique (Willmott and Huber, 2000; Christen and Eres, 2008; Schou, 2009; Marla et al., 2011), substrate and target are mounted in a vacuum chamber at a certain distance and a laser pulse is used to ablate the material from the target. Following ablation, plasma is created and material from the plasma is deposited on the substrate. Generally, deposition can be performed either in a gas atmosphere or vacuum.

Thin films of KBB were produced out of a polycrystalline $K_{0.3}MoO_3$ powder which was pressed in tablets of 20 mm diameter. The target was mounted on a rotating holder opposite to a substrate. Depositions were performed on (1-102) Al_2O_3 (ALO) and (510) $SrTiO_3$ (STO) substrates of 10 x 10 x 1 mm^3 and 5 x 5 x 0.5 mm^3 dimensions. These substrates were chosen because they have suitable parameters for epitaxial growth (J. van der Zant, 1996). Depositions were performed with an excimer KrF* laser (COMPexPro) of a wavelength 248 nm, pulse duration ≥7 ns, repetition rate 2-50 Hz and fluence 0.2-10 J/cm^2. Substrate was mounted on a heater at a typical distance of 5 cm away from the target. Number of pulses was usually 6000, with several attempts at 3000, 9000, 10000 and 15000. After a series of trials we have fixed fluence to 2.4 J/cm^2 and repetition rate to 5 Hz. Depositions were performed in an oxygen atmosphere with pressure (p_{02}) varying between 1-10 Pa and a substrate temperature (*Ts*) between 375-450 °C. Here, we will present the influence of the number of pulses, *Ts* and p_{02} on thickness, stoichiometry and texture of the films on two different types of substrates

Table 1: Thickness *d*, stoichiometry, substrate temperature T_S, oxygen pressure p_{O2}, number of pulses and errors ΔK and ΔO due to measuring technique in K and O fraction of several KBB films from the 7th batch. Some thickness values exceeded limitations of the measuring method.

Film	*d* (nm)	Stoichiometry	*Ts* (°C)	p_{02} (mbar)	No. of pulses	ΔK	ΔO
BB6 ALO	336	$K_{0.24}MoO_{2.86}$	375	0.06 O_2	6000	0.03	0.35
BB5 STO	392	$K_{0.29}MoO_{3.20}$	400	0.08 O_2	6000	0.04	0.40
BB2 ALO	336	$K_{0.28}MoO_{2.82}$	450	0.06 O_2	6000	0.03	0.35
BB9 ALO	294	$K_{0.29}MoO_{3.24}$	450	0.08 O_2	6000	0.04	0.40
BB8 ALO	340	$K_{0.30}MoO_{3.00}$	425	0.08 O_2	6000	0.04	0.42
BB7 ALO	468	$K_{0.19}MoO_{3.15}$	375	0.08 O_2	6000	0.03	0.44
BB2 STO	468	$K_{0.31}MoO_{3.31}$	450	0.06 O_2	6000	0.04	0.46
BB6 STO	468	$K_{0.30}MoO_{3.13}$	375	0.06 O_2	6000	0.04	0.44
BB3 STO	>524	$K_{0.28}MoO_{3.40}$	400	0.04 O_2	9000	0.04	0.48
BB5 ALO	397	$K_{0.27}MoO_{3.39}$	400	0.08 O_2	6000	0.04	0.48
BB11 ALO	>524	$K_{0.31}MoO_{3.25}$	400	0.04 O_2	15000	0.04	0.45
BB12 ALO	184	$K_{0.29}MoO_{3.03}$	400	0.04 O_2	3000	0.04	0.42
BB4 ALO	>524	$K_{0.28}MoO_{3.07}$	400	0.04 O_2	10000	0.04	0.43

Thickness and stoichiometry of some of the deposited films were determined by TOF-ERDA. The films were irradiated with 20 MeV $^{127}I^{6+}$ ion beam and two detectors registered energy of recoiled ions and time of flight of each recoil. Analysis of the results revealed distribution of elements in the examined films and part of the substrate as well as possible contamination of the film.

Imaging using AFM was performed by NanosurfFlex AFM (NorFarb). Linear scanning rate was optimized between 1.5 and 2 Hz with scan resolution of 512 samples per line. Images were acquired in contact mode with silicon and silicon-nitride tips.

RESULTS AND DISCUSSION

In recent years, we have produced seven batches of KBB thin films comprising more than 100 samples by PLD in different conditions.

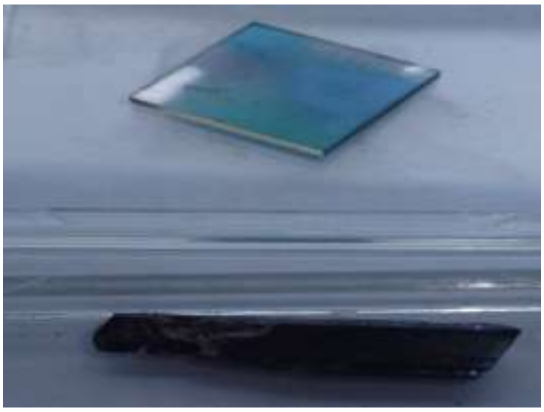

Figure 1: KBB film (above) and crystal (below).

Comparison between a KBB film and crystal is presented in Figure 1.

Results of TOF-ERDA revealed that thickness of the deposited films varied between 100 nm and >524 nm. The results are presented in Table 1 for some of the films. Exact thickness for the thicker films (>524 nm) could not be determined because of the limitations of TOF-ERDA method. As expected, thickness increases with the number of pulses as presented in Figure 2. Atomic ratio of K/Mo and O/Mo in stoichiometry of the produced films does not change significantly with the number of pulses, as presented in Figure 3.

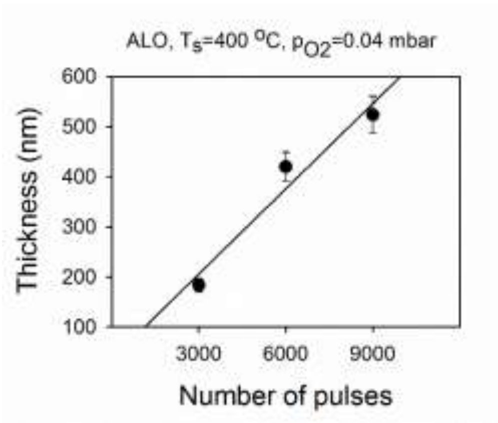

Figure 2: Film thickness versus number of pulses. Line is just guide for the eye. Bars indicate uncertainty in value.

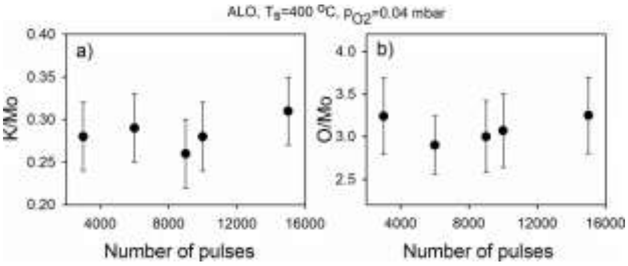

Figure 3: Stoichiometry of deposited films vs. number of pulses for ALO substrate: a) ratio of K/Mo and b) O/Mo atoms. Bars indicate uncertainty in value.

Influence of p_{02} on stoichiometry of the deposited films is presented in Figure 4. We notice that ratios of K and O to Mo follow the same trend for different substrate temperatures *Ts*. Ratio of K/Mo atoms increases up to 0.04 mbar and then it starts to decrease while the ratio of O/Mo atoms increases with p_{02} in the entire range. Similar trend was noticed in (Mantel et al., 1997) for $Rb_{0.3}MoO_3$ films produced by PLD.

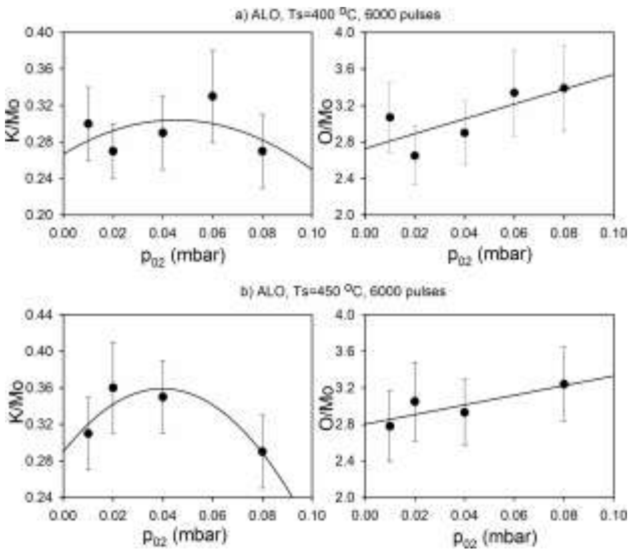

Figure 4: Atomic ratios of K and O to Mo vs. p_{O2} for ALO substrate at a) *Ts*=400 °C and b) *Ts*=450 °C. Lines are just guide for the eye. Bars indicate uncertainty in value.

Influence of *Ts* on stoichiometry of the deposited films is presented in Figure 5. Atomic ratios of K/Mo and O/Mo increase with *Ts* for the films deposited on STO substrate in the entire range, while for the films grown on ALO substrate atomic ratios of these elements start to decrease at 420 °C.

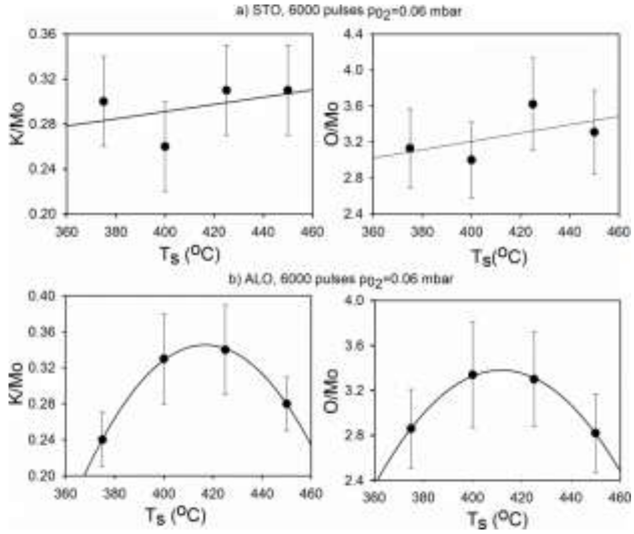

Figure 5: Ratio of K/Mo and O/MO atoms vs. *Ts* for a) STO and b) ALO substrate. Lines are just guide for the eye. Bars indicate uncertainty in value.

AFM revealed that the films were comprised of nanometer sized grains with lengths between 100 and 450 nm and widths between 50 and 150 nm. The films grown on STO substrate exhibited better ordering of the grains than those grown on ALO. Figure 6 represents length of the grains versus *Ts* and p_{02} for different substrates.

The length of the grains decreases with *Ts* down to 425 °C and then it starts to increase for both substrates. For ALO substrates at two different *Ts* the grain length increases with p_{O2} up to 0.06 mbar and then it starts do decrease.

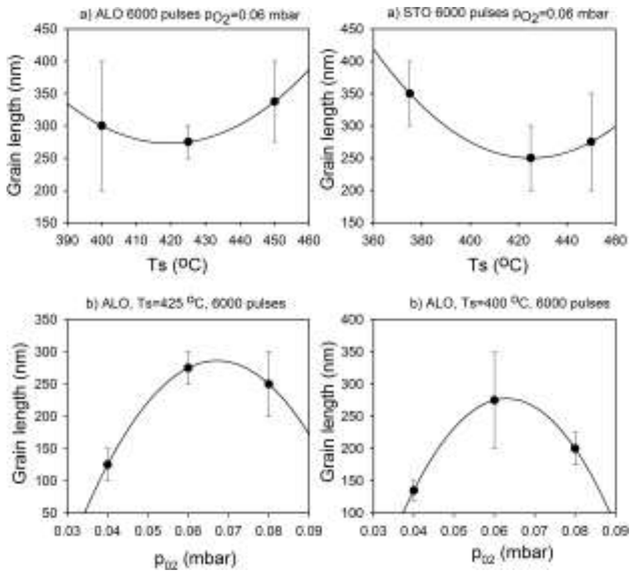

Figure 6: Dependence of the grain length on a) *Ts* for ALO and STO substrates and b) p_{O2} for ALO substrate. Lines are just guide for the eye. Bars indicate uncertainty in value.

CONCLUSION

Based on the analysis of the influence of p_{02} and *Ts* on the quality of the deposited films we were able to determine optimal conditions for the production of KBB films. Other characterization techniques like electrical transport measurements and fs-TRs enabled us to detect transition to CDW state in some of the films. We concluded that the optimal conditions for the production of KBB films are Ts=425 °C and p_{02}=0.06 mbar. Further production of KBB thin films is on the way but this time with a completely different PLD system. New system required optimization of p_{02} and Ts all over again because every vacuum chamber is unique. However, our preliminary results showed that deposition conditions in a new chamber were not that far from our previously established values and we were able to determine optimal p_{02} and Ts very fast. Preliminary results show that we have managed to produce better quality films than before. Further investigation will include the influence of other deposition parameters like repetition rate on the deposited films.

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Summary/Sažetak

Pulsna laserska depozicija (PLD) je postala najvažnija tehnika za proizvodnju novih materijala sa kompleksnom stehiometrijom i višeslojnih struktura. U ovom radu su predstavljeni parametri koji utiču na proizvodnju tankih filmova $K_{0.3}MoO_3$ (KBB) pomoću PLD tehnike. KBB je kvazi-jednodimenzionalni (q-1D) provodnik koji prelazi u novo osnovno stanje sa valom gustoće naboja (CDW) i to na temperaturama nižim od temperature prelaza (Tp). Ovaj sistem se smatra “kanonskim” CDW sistemom i njegova svojstva se intenzivno proučavaju u bulk (masivnim) uzorcima. Proizvodnja tankih KBB filmova posljednjih godina omogućila je istraživanje svojstava CDW –a u uslovima smanjene dimenzionalnosti. Izbor parametara depozicije ima veliki uticaj na proizvodnju filmova te ga je stoga neophodno istražiti da bi se proizveli visoko kvalitetni filmovi. Ovo istraživanje omogućava da se odrede optimalni uslovi za depoziciju KBB tankih filmova PLD tehnikom.

The Pulsed Laser Deposition (PLD) technique uses high power laser pulses (typically ~108 Wcm-2) to melt, evaporate and ionize material from the surface of a target.Â The technique of PLD has been used to deposit high quality films of materials for more than a decade.The technique uses high power laser pulses (typically ~108 Wcm-2) to melt, evaporate and ionize material from the surface of a target. This "ablation" event produces a transient, highly luminous plasma plume that expands rapidly away from the target surface. The ablated material is collected on an appropriately placed substrate upon which it condenses and the thin film grows. Pulsed laser deposition (PLD) is a very simple thin film deposition method which has been successfully used to deposit a wide range of materials such as high-temperature superconducting thin films, optical coatings, magneto-resistive thin films, etc. From: Solar Energy Materials and Solar Cells, 2012. Related terms: Titanium Dioxide. Oxide. Hydroxylapatite. Ion. Pulsed laser deposition (PLD) is a physical vapor deposition (PVD) technique where a high-power pulsed laser beam is focused inside a vacuum chamber to strike a target of the material that is to be deposited. This material is vaporized from the target (in a plasma plume) which deposits it as a thin film on a substrate (such as a silicon wafer facing the target). This process can occur in ultra high vacuum or in the presence of a background gas, such as oxygen which is commonly used when depositing