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Reviewer's report on the doctoral thesis

"Kinetic Monte Carlo Simulations in
Physics of Thin Films: from Growth to Electronic Properties"
by Mr. Vit Gabriel
(Supervisor doc. RNDr. Pavel Kocán, Ph.D.)

1. Scientific context

Pulsed lased deposition (PLD) is one of the main experimental methods to create diverse nanostructures supported by solid substrates. This technique has immense application potential in the fabrication of layered materials, including crystalline thin films, metallic multilayers, ceramic oxides, nitride films, quantum dots etc. which are core elements of modern electronic/optical/magnetic/superconducting systems. Recently, there has been considerable interest in PLD multiferroic materials, especially layered perovskites, which can exhibit the unique combination of ferroelectricity and ferromagnetism. Simultaneous occurrence of the aforementioned pair of properties makes layered perovskites promising candidates in designing and manufacturing of novel magnetic memory systems, microwave filters and magnetic field sensors. One of such perovskite materials are the ABO_3 compounds where A and B are metal cations which are standardly fabricated using the PLD method.

The PLD procedures for the synthesis of layered perovskites involve very complex laser-pulse induced effects generating the material (metal) to be deposited on the substrate (metal oxide). In consequence, the quality of the deposited structure is largely dependent of the process parameters such as the laser fluence, pulse frequency and substrate temperature. These parameters affect seriously the deposition rate, change intervals between the arriving portions of material and modify diffusion of the deposited particles and reconstruction of the growing nanostructure. For these reasons detailed

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understanding of the influence of the external parameters on the PLD deposition/growth is of critical importance to optimization and to improvement of effectiveness of the laser-assisted methods for the fabrication of layered perovskites and similar materials.

In the light of the above arguments, I am convicted that the subject of the PhD thesis by Mr. Vit Gabriel is topical and it focuses on very actual problems related to the epitaxial growth of single-crystalline thin films. Moreover, the theoretical approach adopted by the Candidate, in addition to basic research character has also a direct reference to the experiment, which I consider to be an added advantage.

2. Scientific content of the thesis

The main topic of the thesis is theoretical modeling of the pulsed-laser deposition growth of thin films and polaronic diffusion in the explored systems. To that purpose the Author focused on the $LuFeO_3$ perovskite and developed a coarse grained kinetic Monte Carlo (KMC) model of the corresponding PLD. In my opinion, the main scientific achievement of the Candidate was the original and novel approach to the PLD process, resulting in the significant improvement of the effectiveness of the computational method. With this model it was possible to overcome the usual problems related to modeling of deposits on surfaces, including limited size of the system (surface area) and short deposition time (with one or a few layers reachable in conventional simulations). The key advancement of the proposed PDL theory was the replacement of fast diffusion of the hot deposited material by the unit gas with individual density defined for each layer. According to this useful assumption, the very fast diffusion of deposited species occurring in the experiment was mimicked by the infinitely fast exchange of unit gas between neighboring cells of the modeled ABO_3 surface. The developed KMC model was first validated and calibrated using the literature XRDS data for PLD of $SrTiO_3$ and these calculations allowed for the alternative explanation of the bi-exponential temporal evolution of the coverage, observed in the experiment. To that end the Author postulated the two timescales related to the molecule-surface binding energy and to the energy of intermolecular interactions. The proposed explanation was simpler and straightforward, without having to assume a specific mechanism of the inter-layer transport.

In the next stage of research, the Candidate focused on modeling of the PLD of the hexagonal perovskite $LuFeO_3$, especially on the effect of pulse frequency on the structural properties of the growing deposit. The performed simulations resulted in several interesting observations, which shed light on the dependence of growth parameters such the means surface width (p_j) and the growth exponent (β) on the laser frequency. One outcome which I value highly is the explanation of the discrepancy between the trends in p_{20}-plots obtained from the experiment and from the simulations at constant substrate temperature. As the Candidate found, the assumption of constant temperature made in the simulations, which is also believed to be fulfilled in the experiment, can be incorrect. Accordingly, to reproduce adequately the decreasing trend in p_{20} for increasing pulse frequency one thus has to take into account heating of the surface, induced by the impinging hot deposit. The additional simulations at variable temperature showed that the deposition-induced heating reduced roughness of the modeled surface and this effect was found to be equivalent to the lowered pulse frequency used in the experiment.

Separate calculations with the KMC model were performed to explore the polaronic diffusion in titanium-doped hematite. The Author used the previously developed model to explore the effect of energy barrier for diffusion and electrostatic potential introduced by dopant on the contact potential difference (CPD). A few variants of the model were tested to examine the separate and combined influence of the above factors. These extended simulations demonstrated that the assumption of constant energy barrier for polaron diffusion within the entire system is the best option (model M1). None of the other models, assuming local modification of the lattice properties, revealed to reproduce the experiment better than M1. In conclusion, the Author stated that the effect of titanium doping has more complex origins than the simple decrease in diffusion barriers and/or local change in charge density.

The last application of the KMC simulations presented in the thesis was related to modeling of hole polarons in nickel-doped hematite. In this case, the Author tested the model (M1) to check its ability to describe systems containing positively charged species with lower mobility, as compared to electron polarons. The predicted CPDs were in close agreement with the experimental data and accuracy of the theoretical predictions was further increased by incorporating the effect of random impurities (trapping centers) in the hematite crystal. Moreover, the model was also used to study hole polaron injection, especially to reproduce the decreasing elapsed timed between subsequent injections, visible in the experiment. The proposed charge injection model was found to match the measured data very well. One more important application of the model refers to the time evolution of the outside potential which was calculated based on the measured times between injections.

The main scientific results of the thesis outlined above, that is the formulation of the KMC model of the PLD growth and its further extension to electron and hole polaron diffusion/injection are new with central importance to understanding and predicting of growth and electronic properties of thin films. In addition to that, the findings reported in the thesis have clear application potential in the corresponding experimental methods of synthesis and characterization of thin films (e.g. in optimization of the PLD and doping of thin films). These results were published a few scientific papers, which shows interest of the scientific community in research pursued by the Candidate.

3. Structure and language of the thesis

The thesis is divided into a few main parts, including the short introduction and basic information on the KMC method (Chapter 1). The two next chapters (2 and 3) contain the Author's own results with most important facts about the corresponding experimental procedures and key assumptions of the developed KMC model. At the end of each chapter (2 and 3) details of implementation of the theory were additionally provided. I think that the above layout of the thesis is correct, as it allows to follow easily the Candidate's idea to proceed from the simpler (PLD) to more complex processes (polarons). What helps a lot in detailed understanding of how the KMC works are the aforementioned implementation details. The conclusions of the thesis are clear and they are supported by the obtained findings.

The language of the work is clear and intelligible. The hypotheses and arguments used for their verification were formulated in a convincing manner. The thesis as a whole is logically consistent and it demonstrates the position of the Author's research in the field with clear indication of the new contribution and advancements. The graphics, including plots and schemes are plain and not overloaded with data.

4. Scientific qualifications of the Author

With the PhD thesis, Mr. Vit Gabriel clearly demonstrated the ability for creative scientific work. This was proven by the critical thinking and independence of the Candidate, which can be easily noticed when reading the thesis. He was able to formulate precisely important problems of the PLD, create suitable theoretical tools and solve these problems in a systematic way. Mr. Vit Gabriel showed that he is sufficiently familiar with main experimental and theoretical methods relevant to his studies. The Author correctly assessed the importance of his research in a broader context of existing knowledge in the field. Limitations of the proposed model and discrepancies between the simulations and experiment were explicitly discussed and possible sources of these effects were proposed. The Candidate used correctly the literature sources and critically placed his findings in the light of these previous studies.

5. Questions and comments for the defense

1. The experimental PLD technique is known to suffer from a few undesirable effects, including non-uniform size distribution of the ablated material (exfoliation, expulsion, sub-surface boiling etc.). Is it possible to modify easily the KMC algorithm to include the non-uniform distribution of the deposited

particles? How this heterogeneous mass transport to the surface would affect the simulated quantities, such as coverage, XRDSs and growth parameters p_{20} and β ?

2. In the simulations of PLD for the hexagonal perovskites triangular lattice of cells was used (as shown in Figure 2.3). However, the modeling of polarons in hematite was performed on a square lattice. Can the Author explain which specific crystal face of hematite corresponds to this lattice and how this choice can be justified?

3. Is the proposed model of polaronic diffusion general in terms of the dopant size and chemistry? In particular, can the Author comment on the effect associated with the size of the dopant atoms on the possible distortion of the hematite lattice. Would there be any relation of the dopant size and the number of generated structural defects (modifying the ideal square lattice assumed in the simulations)?

4. Did the Author attempt to measure fractal dimension of the deposited surfaces. Would it be simple to correlate this quantity with the laser pulse frequency?

5. Technical: In some of the figures (e.g. Fig. 2.1) coloring of the lines is not explained which makes interpretation of the data difficult.

6. Final conclusion

To sum up, in my opinion, the PhD thesis by Mr. Vit Gabriel presents original research results which are characterized by originality, novelty and clear applicability. The Candidate showed all of the qualifications needed for pursuing creative scientific work. Thus, I am convinced that Mr. Vit Gabriel deserves the PhD title and I recommend the thesis for defense.