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Advanced complex oxides thin films deposition technique

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In this paper I present my understanding of the deposition of the complex oxides thin films and heterostructures by using layer-by-layer Molecular Beam Epitaxy system.

Complex oxides represent a vast class of materials with rich physical properties. In additional new functionalities can be obtained on the interfaces between different oxide layers. To understand unique physical and chemical properties of complex oxides including high temperature superconductivity, colossal magnetoresistivity, multiferroic behavior etc. one need appropriate deposition technique which allows to synthesis these materials. Indeed the deposition technique allows the rational design of materials via the design of metastable artificial layered structures and understanding the principles of chemical reactions within single atomic layer and formation complex oxides layered crystal structure with unique physical properties.

There is a variety of deposition methods including thermal and e-beam co-evaporation sputtering, thermal or laser molecular beam epitaxy (MBE), on-axis and off axis high-pressure sputtering, on-axis and off-axis pulsed laser ablation, etc [1]. Our preference is Molecular Beam Epitaxy (MBE) [2]. The MBE growth technique has major advantage – a precise control of composition and lowest kinetic energy of impinging atoms compared with all other methods. The latter reduces possible interface atoms intermixing. These deposition capabilities allow us to do deposition of different atomic layers with precision less than one unit cell size in different sequences and to do selective doping of single atomic layers.

Let us describe the main concept of the research MBE system configured for oxide applications. The system is based on silicon-style architecture which provides the optimal design of load locks, transfer and vacuum system developed for semiconducting MBE. The difference is the operation of critical parts (sample manipulator, effusion cells, etc.) under extreme conditions i.e. in aggressive oxygen atmosphere and at high temperature [3,4]. The ultra high-vacuum chamber must contain the optimal number of oxygen resistive effusion cells (typically eight) which can be used for different elements and provide flexibility in composition. Optionally the system should have e-gun evaporation system for those elements which can not be evaporated by using effusion cells. The sources are equipped with shutters which are controlled by computer and the time of being source open determines the amount of atoms deposited on the substrate. The atomic beams are controlled by quartz crystal monitor (QCM). The layer-by-layer MBE hinges on an accurate knowledge of the absolute deposition rates. Once the absolute rates are known, the mechanical shutter can chop the atom beams and deposit in one burst exactly one atomic layer of the element involved. A pure ozone beam is the most reactive due to extreme instability of ozone molecules what enables sufficient oxidation under high vacuum conditions. This permits in-situ monitoring of the surface structure by reflection high energy electron diffraction (RHEED).

This oxide MBE system enables growth of complex oxides compounds based on traditional block-by-block and co-deposition schemes [5] as well as further develop the layer-by-layer deposition based on the dosage of the constituents on the level of the single atomic layer.

This approach has several advantages including control of termination of the substrates, sequence control and doping within one atomic layer. In additional together with in-situ crystal structure RHEED control and layer-by-layer deposition schemes it is possible to investigate the chemical reaction at the surface by precise dosage of elements involved.

The critical challenge to do layer-by-layer deposition of complex oxides is related to the way how to control the amount of deposited atoms of metals and their oxidation. The typical deposition flux rate is 10^14 atoms/s cm^2 and we need the precision of measurement at least better than 1%, what corresponds to less 10^12 atoms/s cm^2. Also this precision is not sufficient because after repetition of the atomic layers deposited with the error the secondary phase precipitates can be nucleated due to the error propagation. There are several experimental methods which can be used for real time control of deposition flux including atomic absorption spectroscopy [6], electron impact emission spectroscopy [7], beam flux monitoring [8], etc. All these methods are element sensitive and can not provide sufficient performance for measuring deposition rates of different metals. The main advantage of real time flux measurement is flux control during thin film deposition. The disadvantage of this usage is that the systematic error is substantial during deposition of a single atomic layer and it also propagates during the film growth. According to my experience no one method is as universal as QCM. However QCM normally is used as preliminary flux calibration, which is valid only under assumption that the flux is stable during all growth process. Therefore further improving sensitivity and developing of new real time flux control methods is mandatory.

The operational temperature of modern effusion cells can be stabilized better than one degree of Celsius that provides necessary stability of deposition fluxes in vacuum. When the effusion cell is working in aggressive oxygen atmosphere additional attention should be taken to provide the differential pumping of each effusion cell to reduce oxidation of the evaporated metal and increase operational time. The disadvantage of the oxide MBE system with effusion cells only is limiting number of elements can be deposited. The elements with extreme high melting points can not be deposit by using effusion cells. One needs to use the other metal source i.e. the e-beam evaporator, which unfortunately has not stable deposition flux. The development of the new type of evaporation sources with stable fluxes for wide class of elements including metal with high melting points is one of the critical requirements for the future development of oxide MBE system.

Independently on the way how we obtain the flux deposition rate based on QCM measurement or one of the real time methods we need the real time correction of the deposition time because of insufficient precision of initial calibration. According to the present state of the art the only method which can give the adequate feedback is in-situ RHEED which is extremely sensitive to surface crystal structure and nucleation of secondary phase precipitates and can provide useful hints about the nonstoichiometry at the earlier stage of the film growth. To have real time growth control it is necessary to do analysis of the evolution of the RHEED image during the film growth. Normally the bottleneck of this analysis is the complicate time dependence of the RHEED image during the growth of the complex oxide thin film based on layer-by-layer method. Understanding the evolution of the RHEED image during the growth is the key to the successful deposition of high quality complex oxides thin films and heterostructures based on the layer-by-layer MBE deposition method.

A layer-by-layer oxide MBE technique is unique experimental method itself to study principles and driving mechanisms of formation of complex oxides compounds on a single atomic layer basis. Most of complex oxides are ionic materials and principles which are using in structural chemistry can be applied as a starting point. However the difference is that we can observe the initial reconstruction after deposition of a single atomic layer in a real time, which is caused by formation of electrically neutral surface structure. In case if the formation of single atomic layer is forbidden due to energetic reasons the RHEED image analysis immediately validate the distorting of the surface via reduction of the RHEED specular reflection intensity due to surface roughness and formation of three dimensional precipitates. Further development of first principles of synthesis of complex oxide materials based on layer-by-layer deposition schemes is necessary.

So far, the oxide MBE has been successfully used to deposit single thin films of a variety of cuprates, titanates and manganites. The next step was successful fabrication of heterostructures with atomically abrupt interfaces including trilayer Josephson junctions, SQUIDs, and spin-polarized tunnel junctions. Recently the realization of the different electronic states in the interfaces between different oxides blocks opened the new avenue in engineering complex materials [9-12]. The new perspective is the design of electronic materials on an atomic scale in order to achieve desired property and/or a new functionality.

In summary the principles of layer-by-layer oxide MBE deposition technique has been presented. The main advantage of this method is that in addition to the deposition of single thin films of variety complex oxides and heterostructures this technique has future perspectives to grow artificial metastable structures with new properties and functionalities. This layer-by-layer deposition technique allows engineering of electronic materials by artificial stacking of compatible single atomic layers under oxidation environment. Further development of the instruments for real flux monitoring with high precision and design of stable evaporation sources for broad range of elements is necessary for future perspectives of the complex oxides.

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