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Oxygen Engineering; a Tool for Property Manipulation

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Abstract Oxides which forms the vast majority among the materials of the earth's outer crust, are an important class of materials. They harbour materials with a wide span of properties which could be exploited for many technological applications. Oxides have complex crystal structure compared to metals or semiconductors. Oxygen plays a very important role in the determination of the properties of the oxide materials. Controlling the oxygen content or 'oxygen engineering' could result in manipulating the properties of a oxide material and key to that is the use of innovative synthesis technique like reactive molecular beam epitaxy. One would expect our electronic devices to be loaded with more and more oxide materials in the near future to achieve devices with superior performance and added functionalities in the decades to come. It will not be surprising even to think of an all oxide devices making its way to the electronics industry as research on oxide materials develops further.

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Oxides are an important class of materials which harbours an array of intriguing properties. They have more complex crystal structures compared to usual metals or semiconductors. One can find in these class of materials from insulators, semiconductors, metal like conductors to superconductors to name a few. As the probing instrumentation becomes better with time, more and more information is gathered and hence, a deeper understanding of the oxide materials is developed. This has led to the discovery of many exotic phenomena and has opened up the possibility of technological application in electronic devices with advanced functionalities. We live in a world dominated by technology hungry devices constantly demanding miniaturization and the inclusion of more functionalities. Oxide materials are the direction in which materials scientists look to answer these increasing demands. Of course the research on oxides is challenging, but it also brings new opportunities. One can find quite a lot of review articles in scientific literature on the emerging technological applications of oxide materials.

For the past two three decades, the research on oxide materials has produced a wide range of results. The development of Si based semiconductor technology has revolutionised the electronic devices that we use today and the advent of new advanced oxide materials are proving to add even more functionalities to it. The discovery of superconductivity in ceramic oxide materials quarter of a century back, has led to a flurry of research activity and that has in some sense resulted to the better understanding of complex oxides and the discovery of many exotic phenomena in these class of materials. Even though, most of the studies have originated from the bulk synthesis of these materials, thin film synthesis has opened up new horizons in this filed.

The observation of interface related phenomena like high mobility two dimensional electron gas (2DEG)at the interface of two insulators (Ohtomo and Hwang 2004), ferroelectricty(Bousquet et al. 2008), superconductivity (Reyren et al. 2007), magnetism (Brinkman et al. 2007) are fair examples to name a few. The observation of high mobility 2DEG at the interface of $LaAlO_3$ thin film grown on TiO_2 terminated $SrTiO_3$ substrate (TiO_2-LaO interface) generated tremendous research interest. It is worthwhile to state that the oxide thin film synthesis is evolving to the extent that it is possible to deposit films with atomically sharp interfaces with control over a monolayer in some cases.Best examples are the conducting/insulating stacks $SrTiO_{3-ä}/SrTiO_3$ heterostructures with varying thicknesses (Muller et al. 2004) and the observation of metal-insulator transition with heterostructure layer thickness in $LaAlO_3/LaNiO_3$ stacks(Boris et al. 2011).

When discussing about oxides, it is widely accepted that the oxygen stoichiometry plays an important role in determining the properties of the material. Of course, the role played by oxygen in $YBa_2Cu_3O_{7-ä}$ superconductor is well known to high temperature superconductor researchers; the oxygen stoichiometry (oxygen induced doping) transforms the material from an insulator to a superconductor. Also, for the electron doped superconductor $Nd_{2-x}Ce_xCuO_{4+ä}$, the presence of very minute amount of additional oxygen at the apical site is believed to inhibit superconductivity (Krockenberger et al. 2013). It was well known for some time that oxygen vacancies can play a vital role in shaping the properties of an oxide material. Strontium titanate crystal, an old diamond substitute, if some of the oxygen atoms are removed from the crystal, the glittering gem turns to a dull blue crystal (Mannhart and Schlom 2004). These oxygen vacancies also turn the insulating crystal to a conducting one. The creation of oxygen vacancies in $SrTiO_3$ can be achieved by high temperature vacuum annealing (vacuum annealing at higher temperature can result in oxygen removal or in other words the creation of oxygen vacancies in the resulting crystal matrix). In simple terms, one can imagine that the removal of an oxygen atom removed from an oxide crystal is like adding two electrons to the crystal matrix, thus acting like electron donating dopants. In semiconductors, doping is achieved by the partial substitution of one element with another element of different valance state. The oxygen vacancy generated doping has an advantage over the element substitution type of doping as no additional element is introduced, which makes the process simple. Also the introduction of additional element could invite unintended issues like chemical compatibility, for instance. Hence, in principledoping a material just by the tuning of oxygen content is very promising. But in practise, it is much difficult to tune the oxygen content in a material in a controlled and reproducible manner. However, there has been progress in achieving this by reactive molecular beam epitaxy (RMBE) technique. At the time of discovery of high temperature superconductivity in cuprates itself, scientists believed that MBE could be an ideal synthesis technique for the synthesis of new complex oxides. At that time MBE technique has already evolved as a dominant technique for the preparation of high quality thin films in the semiconductor area. But,the transforming the semiconductor MBE system for the growth of oxide materials has proved to be challenging. However, over the decades many of the challenges in the area were overcome and RMBE has proved to produce high quality thin films of many complex oxides. Still it is far from being perfect. Various research groups in Japan, Germany and USA are putting a great deal of effort to improve the instrumentation of RMBE to match the quality and success of semiconductor MBE systems. It is worth to mention that the oxide MBE technique has already proven to grow high quality thin films of various complex oxides by now(Karimoto et al. 2001, Tsukada et al. 2002, Bozovic et al. 2002, Kurian and Naito 2004, Brooks et al. 2009, Buckow et al. 2012). Most remarkable point is that the RMBE could be used as a synthetic synthesis technique for the synthesis of new materials which otherwise cannot be accessed by conventional synthesis techniques (Alff et al. 2011).

Having mentioned the role of RMBE in the synthesis/growth of oxide thin films, one has to keep in mind that all the constituent elements required for the synthesis of a material is supplied as elemental or molecular species separately in MBE technique((Alff et al. 2011). Hence, in the case of oxide thin films, oxygen species is supplied separately which allows the possibility of controlling the oxygen content in the material during film deposition. It was mentioned earlier that oxygen content plays a vital role in shaping the properties of an oxide material and 'engineering' the oxygen content in an oxide material would eventually result in the tailoring of the material properties. Recently, it has been demonstrated by RMBE that it is indeed possible to engineer the oxygen content in an oxide material in a reliable and reproducible way; oxygen engineering of a seemingly simple oxide like hafnium oxide, one could tune the electrical transport properties of hafnium oxide from an insulator to a conductor. Hafnium oxide is significant as it has already made it way to the silicon based electronic industry as a high-k dielectric and has demonstrated its compatibility with semiconductor fabrication process. Intentional controlled introduction of oxygen vacancies in hafnium oxide thin films by RMBE, it was demonstrated that the bandgap of the material could be varied over 1 eV and the electrical conductivity could be varied from an insulator to a conductor (~400 micro ohm at room temperature) (Hildebrandt et al. 2011, Hildebrandt et al. 2012). Even though it is only the first step towards the real exploitation of this technique, the most interesting point is that one could explore the use of such films for technological applications straightaway. Before coming to this point, it is worth to mention that the rapid miniaturisation and demand for high capacity memories in digital devices has pushed researchers to investigate various options to fulfil the demand for low power, high density non-volatile random access memories (RAM). Among the various technologies under consideration, one of the major areas of research is in the resistance switching random access memories (RRAM). In short, RRAMs are general a capacitor like metal-insulator-metal (MIM) stack structures where the resistance of the sandwiched insulating oxide is varied by the application of an electrical stress. In order to make such a structure to perform stable switching operation, the pristine RRAM devices often requires an initial electroforming process involving the application of a 'forming' voltage which is higher than the operating voltage (Waser and Aono 2007).This electroforming process can be interpreted as an electric field induced controlled soft breakdown which involves many phenomena resulting in the formation of conducting filaments involving the drift of oxygen or metal ions in the switching layer. The subsequent switching operation can be understood as the making and breaking of the filament at the weakest point by the movement of ionic species leading to a low and high resistance states. The forming process employed in here, introduces oxygen vacancies in the virgin state leading to the formation of conducting filaments. In this case, the making and breaking of the conducing filaments and hence the low and high resistance states occur due to the movement of the oxygen ions. The forming process which requires high electric fields and this leads to variations in the device characteristics and hence forming free or low forming voltages are desirable for practical applications of RRAM. If one can introduce oxygen vacancies in the insulator layer during deposition process, the forming voltages could be considerably reduced or even eliminate the forming process (forming free) altogether.(This would ultimately mean that the forming voltage and the operating voltages being in the same range.)

Now we consider the case of earlier mentioned oxygen engineered hafnium oxide thin films for such RRAM devices. One would naturally expect that the oxygen engineered hafnium oxide used as the sandwich layer could lead to an easy forming process. The studies using oxygen engineered hafnium oxide thin films has shown that one can make almost forming free RRAM devices (Sharath et al. 2014a). In general, the forming voltages are known to increase with sandwich insulator layer thickness in the MIM stack. Even though it is easy to perform forming step in thinner films as it requires only lower voltages, it also adds stringent requirements for the film quality. For thicker films this is somewhat relaxed, but then the forming procedure could become difficult as the forming voltages would reach unacceptable higher values. If one is able to tailor the amount of oxygen vacancies in the insulator layer during deposition, this could lead to the reduction of forming voltages even for thicker films. Sharath*et al*. has succeeded in demonstrating this by using oxygen engineered hafnium oxide thin films with various thicknesses and showed that the forming step could be achieved by low forming voltages. For hafnium oxide thin films with high oxygen vacancy concentration, they have observed a thickness independent forming voltage (Sharath et al. 2014b) which makes it even more interesting for technological applications. Even the observed constant forming voltage was due to the re-oxidation of the top surface of the oxygen engineered hafnium oxide thin films due to exposure to the ambient before the deposition of the top electrode. This would imply that an *in situ* step in the top electrode deposition without breaking vacuum would even result in a perfectly forming free RRAM device obtained through oxygen engineering of the sandwich insulator layer by the RMBE technique.

To conclude, oxides are an interesting class of materials which harbour a wide range of intriguing properties which could be exploited for future technological applications. RMBE which is a thin film synthesis technique can serve as a vital tool for the synthetic synthesis of new materials which are otherwise inaccessible by conventional synthesis techniques. This opens up new horizons for property manipulation by tailoring the stoichiometry of the material in the desired direction. Oxygen engineering of a seemingly simple oxide like hafnium oxide by RMBE in tuning the electrical transport properties in a wide range is a good example of the capability of RMBE as a vital tool for metastable material synthesis. As it was earlier mentioned that the vacuum annealing of a strontium titanate crystal at 800 to 1000 ºC for a few minutes could result in the creation of oxygen vacancies and hence the change in characteristics. However, in contrast such a vacuum annealing at 1000 ºC for 48 h of a stoichiometric hafnium oxide film does not create any notable changes which highlights the power of RMBE as a powerful tool for oxygen engineering of oxide thin films. The thin film synthesis approach also makes the technological application studies of such laboratory level research easy. One would expect our electronic devices to be loaded with more and more oxide materials in the near future to achieve devices with superior performance and added functionalities in the decades to come. It will not be surprising even to think of an all oxide devices making its way to the electronics industry as research on oxide materials develops further.

References

Ohtomo A, Hwang HY (2004) A high-mobility electron gas at the $LaAlO_3$/$SrTiO_3$heterointerface. Nature.427: 423

Bousquet E, Dawber M, Stucki N, Lichtensteiger C, Hermet P, Gariglio S, Triscone J, Ghosez P (2008) Improper ferroelectricity in perovskite oxide artificial superlattices. Nature. 452: 732

Reyren N, Thiel S, Caviglia AD, Kourkoutis LF, Hammerl G, Richter C, Schneider CW, Kopp T, Rüetschi AS, Jaccard D, Gabay M, Muller DA, Triscone JM, Mannhart J (2007) Superconducting interfaces between insulating oxides. Science.317:1196

Brinkman A, Huijben M, van Zalk M, Huijben J, Zeitler U, Maan JC, van der Wiel WG, Rijnders G, Blank DHA, Hilgenkamp H (2007) Magnetic effects at the interface between non-magnetic oxides. Nature Materials. 6 : 493

Muller DA, Nakagawa N, Ohtomo A, Grazul JL, Hwang HY(2004) Atomic-scale imaging of nanoengineered oxygen vacancy profiles in $SrTiO_3$. Nature. 430: 657

Boris AV, Matiks Y, Benckiser E, Frano A, Popovich P, Hinkov V, Wochner P, Castro-Colin M, Detemple E, Malik VK, Bernhard C, Prokscha T, Suter A, Salman Z, Morenzoni E, Cristiani G, Habermeier HU, Keimer B (2011) Dimensionality Control of Electronic Phase Transitions in Nickel-Oxide Superlattices . Science. 332: 937

Krockenberger Y, Irie H, Matsumoto O, Yamagami K, Mitsuhashi M, Tsukada A, Naito M, Yamamoto H (2013) Emerging superconductivity hidden beneath charge-transfer insulators. Sci. Reports. 3: 2235

Mannhart J, Schlom DG (2004) Semiconductor Physics : value of seeing nothing. Nature. 430:620

Karimoto S, Yamamoto H, Greibe T, Naito M (2001) New Superconducting $Sr_2CuO_{4-ä}$ Thin Films Prepared by Molecular Beam Epitaxy. Jpn. J. Appl. Phys. 40: L127

Tsukada A, Greibe T, Naito M (2002) Phase control of La2CuO4 in thin film synthesis. Phys. Rev. B. 66: 184515

Bozovic I, Logvenov G, Belca I, Narimbetov B, Sveklo I (2002) Epitaxial strain and superconductivity in La2"xSrxCuO4 thin films. Phys. Rev. Lett. 89:107001

Kurian J, Naito M (2004) Low Microwave Surface Resistance in $NdBa_2Cu_3O_{7-ä}$ Films Grown by Molecular Beam Epitaxy Jpn. J. Appl. Phys. 43: L1502

Brooks CM, Kourkoutis LF, Heeg T, Schubert J, Muller DA, Schlom DG (2009) Growth of homoepitaxial SrTiO3SrTiO3 thin films by molecular-beam epitaxy. Appl. Phys. Lett. 94: 162905

Buckow A, Kupka K, Retzlaff R, Kurian J, Alff L (2012) MBE growth of $LaNiBiO_{1-x}$ thin films. Appl. Phys. Lett. 101: 162602

Alff L1, A. Klein, P. Komissinskiy and J. Kurian, Ceramics Science and Technology vol. 3 (2011) . Riedel R and Chen IW (ed), Weinheim: Wiley–VCH. pp 269–89.

Hildebrandt E, Kurian J, Muller MM, Schroeder T, Kleebe HJ, Alff L (2011) Single-Oriented Highly Epitaxial CeO_2 Thin Films on *r*-Cut Sapphire Substrates

Hildebrandt E , Kurian J, Alff L (2012) Physical properties and band structure of reactive molecular beam epitaxy grown oxygen engineered HfO2±x. J. Appl. Phys. 112 : 114112

Waser R, Aono M (2007) Nanoionics-based resistive switching memories. Nature Materials. 6: 833

Sharath SU, Bertaud T, Kurian J, Hildebrandt E, Walczyk C, Calka P, Zaumseil P, Sowinska M, Walczyk D, Gloskovskii A, Schroeder T, Alff L (2014) Towards forming-free resistive switching in oxygen engineered $HfO_{2"x}$. Appl. Phys. Lett. 104: 063502.

Sharath SU, Kurian J, Komissinskiy P, Hildebrandt E, Bertaud T, Walczyk C, Calka P, Schroeder T Alff L (2014) Thickness independent reduced forming voltage in oxygen engineered HfO_2based resistive switching memories. Appl. Phys. Lett. 105: 073505.