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Effect of Substrate on Structural, optical and electrical properties of $CuCrO_2$ nanothinfims by Reactive dc magnetron sputtering

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Abstract

Copper chromium oxide thin films have been deposited on glass, sapphire and mica substrates by dc magnetron sputtering method at substrate temperature 200^{0}C. The structural analysis of the deposited films with GAXRD shows the (0 1 2) prominent reflection peak of CuCrO2 with vertical to c-axis as delafossite structure and surface morphology was studied by SEM. The optical and electrical properties of the films were studied by UV-Vis spectroscopy and Four probe resistivity measurements. The optical Transmission curves reveal that the film deposited on glass substrate has high transmittance with maximum band gap energy Eg 3.02 eV. The electrical resistivity values were found minimum in sapphire.

Keywards:CuCrO2 thin films,GAXRD, delafossite structure, SEM, band gap and resistivity.

1. Introduction

Past decade, scientists have been focused more research on nano materials because their material properties significantly changes in large scale [1]. There are many different views included in nanotechnology among them, understand and control the structure and composition at nm scale play an important role to make new functional materials and devices. Every manufactured product through nano technology make us to know as faster, lighter, stronger, smarter, safer and cleaner. The development in thin film technology proved that transparent conductive oxides is a group of materials with unique physical properties with wide band gap (>3.1 eV) and electrical conductivity of the order of 10^4 S cm^{-1}. Transparent conducting oxides (TCOs) combine electrical conductivity and optical transparency in a single material [2]. Therefore, TCOs have numerous potential applications including solar cells, flat panel displays, electromagnetic shielding devices, light-emitting diodes, and transparent heat sources [3]. The most popular wide band gap TCOs currently available exhibit n-type characteristics. However, p-type wide-band gap TCOs have not been investigated thoroughly [4,5] basically demand to realization p-n junction devices. There are p-type wide-band gap TCOs materials with the basic formula AMO_2, where, A is a monovalent cation, such as Cu or Ag, and M is a trivalent metal ranging from Al to La which have delafossite structure. Among all the Cu-based delafossites, CuCrO2 has a higher electrical conductivity than the others [6]. After the successful preparation of CuAlO2 film{7] , researchers have developed different TCO thin-films with variuos deposition techniques. The delafossite materials such as CuCrO2 thin films can be deposited using pulsed laser deposition [8–12], chemical vapor deposition [13], and the sol–gel method [14-20].

In present work Cr doped CuO thin films were deposited on glass, sapphire and mica by dc magnetron sputtering method and the effect of substrate on structural, optical and electrical properties have been studied.In minimising the deposition rate is a major problem in sputtering posion of target is adjusted.

2. Experimental Details

Pure Cr (99.99%) and Cu (99.99%) imported from China were used as the sputtering targets of 2 inch diameter and 3-4 mm thickness were deposited onto well cleaned Glass, Sapphire and Mica substrates (75mm X 25mm X 1mm) by reactive dc Magnetron Sputtering System (VR Technologies, Bangalore). High purity Argon (99.999%) and Oxygen (99.99%) gases were used as the sputtering gas and reactive gas respectively in chamber. The substrates were cleaned initially by soap water and dried then dipped into the chromic acid for 24 h, then cleaned with de-ionized water and then cleaned with acetone followed by the Ultrasonic heating. The reactive chamber was pumped to a base pressure of $8x10^{-6}$ m-bar before deposition and working pressure is maintained as $3\text{-}5x10^{-3}$ m-bar. The chamber pressures were monitored with Pirani-Penning gauge combination. The films were grown in the ambient Ar and Oxygen gases flow of 30sccm and 2sccm respectively which were monitored in the Mass flow controllers(Model GFC17, Aalbarg) imported from Germany. The powers of the targets were maintained at 100W and 8W for Cu and Cr respectively with the target to substrate distance was 50mm. The deposition time was around 30 minutes for all the samples. The crystal structure of the samples was studied by the XRD analysis where the CuKα1 radiation was used as a source (λ= 0.154056 nm) in the 2θ range 20^0-60^0. Field Emission -Scanning Electron Microscopy (FE-SEM) was used to reveal the deposition uniformity on surface of the films. The optical transmittance and reflectance were recorded using a Hitachi U-3400 UV–visible–near infrared (UV-Vis-NIR) double beam spectrophotometer in the wavelength range of 300–800 nm.Four probe technique and Hall measurements of the deposited film for electrical properties.

3. RESULTS AND DISCUSSION

3.1. Structural studies:

3.1.a. XRD Analysis

GAXRD patterns of $CuCrO_2$ thin films deposited on different substrates are shown in figure1.The peaks in the spectra of copper chromium oxide thin films deposited on glass, sapphire and mica substrates confirm the structure as the rhombohedral (space group R_3m) delafossite structure of 3R-CuCrO2 is based on trilayer sheets comprised of Cr ions occupying the octahedral holes between two close packed layers of O ions which is good agreement with (JCPDS #89-6744) diffraction peaks. The peaks (006),(101),(012) and (104) in XRD pattern of all substrates have strong grain growth. The narrow full width at half maximum (FWHM) of the deposited CuCrO2 films peaks represented a good crystallinity.

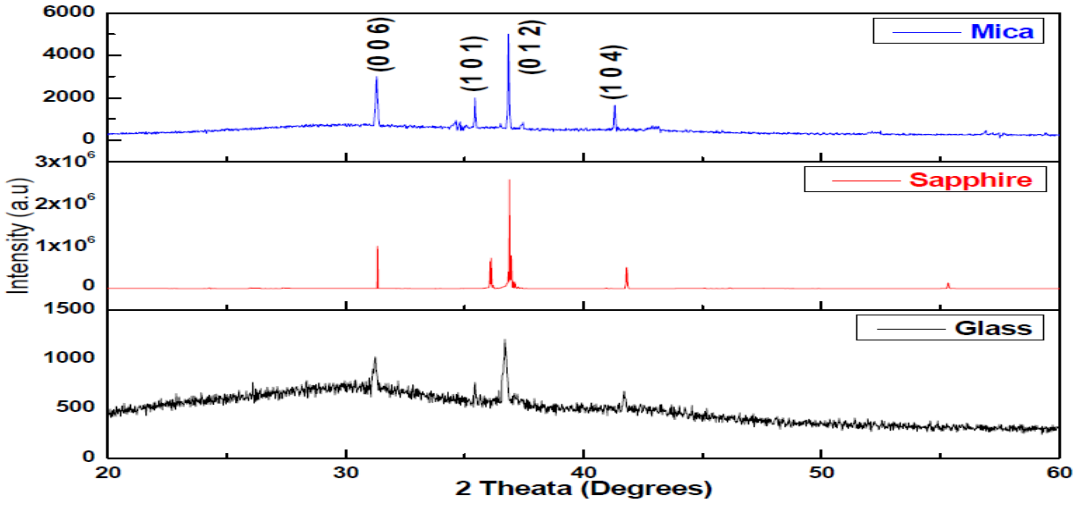

Fig.1. GAXRD patterns of CuCrO2 films grown on different substrates.

The lattice constant variation with substrate material is found due to the structural changes induced by film deposition along with improvement in the composition, which modifies the density of native defects and hence the structural quality of the films. The full width at half-maximum (FWHM) can be used to estimate the crystallite size along c-axis, based on the XRD results shown in fig.1. The mean grain size (D) of the particles was determined from the XRD line broadening measurement using Scherrer equation,

$$D=0.89\lambda / (\beta Cos\theta)$$

Where λ is the wavelength (Cu Kα), β is the full width at the half- maximum (FWHM) of the CuCrO2 (012) line and θ is the diffraction angle. Crystallite size was found as 33.05, 36.63 and 34.64 nm for the film of substrates glass, sapphire and mica respectively .The variation of lattice parameter as a function of different substrates is shown in Table.1.

Name of the Substrate	**Lattice Parameters (nm)**		**Crystallite Size (nm)**	**Strain (line-2-m-4)**
	a	**c**		
Glass	0.2723	1.612	33.06	$7.984x10^{-3}$
Sapphire	0.2846	1.659	36.63	$1.007x10^{-3}$
Mica	0.2789	1.651	34.64	$1.593x10^{-3}$

Table1.Lattice parameters, crystallite size and Strain in the CuCrO2 films deposited on Glass, Sapphire & Mica Substrates.

The From GAXRD analysis it is concluded the presence of a compressive stress and strain in the CuCrO2 films which is characteristic for films prepared by sputtering techniques. The origin of strain can be attributed to structural imperfects at the substrate and thermal mismatching of film and substrate. The compressive residual strain is found different for different substrate. The strain developed in films effects the valence bands due to the positions of their band edges in the Brillouin zone. Also, the substrate movement can cause the growth strain induces in the films. Nucleation and binding of growth species may vary due to the movement of substrate. This affects crystalline quality as well as electrical and optical properties of CuCrO2 films.

3.1.b. Surface morphological analysis

Fig.2(a-c).shows the FESEM images of CuCrO2 thin films deposited on glass, sapphire and mica substrate. As the deposition with different substrates, greater mobility and diffusion effects for species on the surface and affording better nucleation and Cu-Cr-O atoms deposited and more nuclei sited will be generated and a large number of small grains will grow, leading to a smaller-grain structure. The surface morphology of films was analyzed and found the distribution is well in case of Sapphire substrate and good adherence with substrate was observed. FE-SEM images shown in Fig. 2(a-c) revealed that the grains are good adherence with the all substrates and well agglomerated CuCrO2 films.

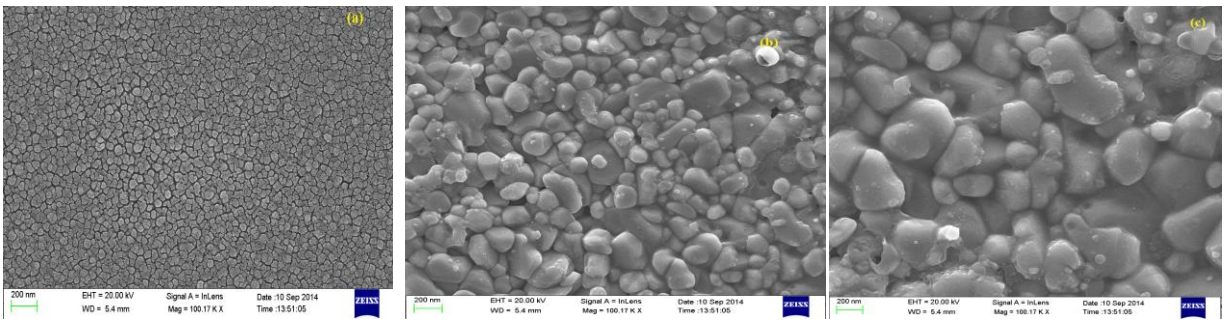

Fig.2. FESEM images of CuCrO2 thin films deposited on Glass, Sapphire and Mica substrate.

3.1.c. Compositional analysis:

The compositional analysis of the experimental CuCrO2 films was carried out using the EDAX measurements in order to know the elements present and its atomic percentage. Fig.3 shows the EDAX plots of CuCrO2 films prepared for different substrates. It could be evidenced from the figure 3(a-c) that all the deposition substrates had a significant influence on the stoichiometry of the films. The deviation of stoichiometry is found in all the substrates might be due to the thermal mismatching of surface of substrate.

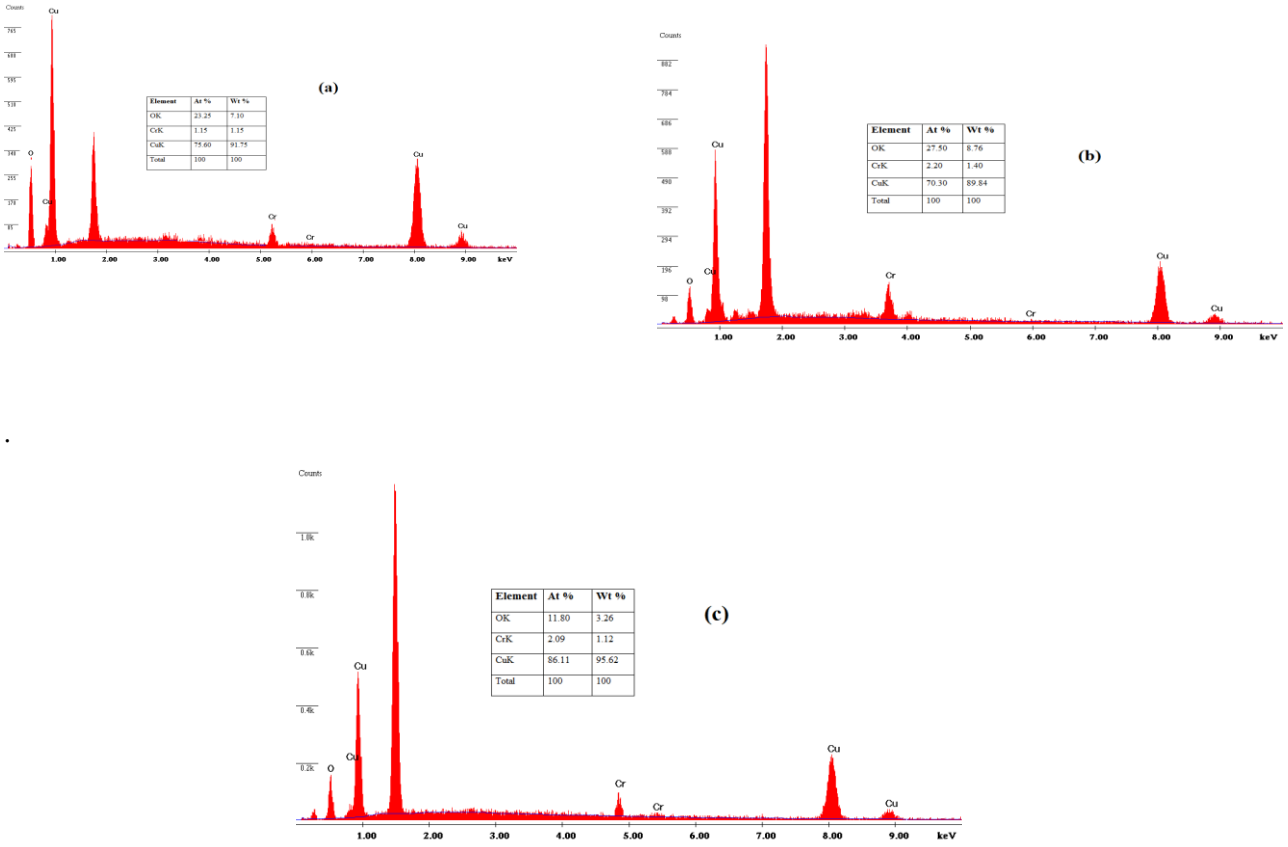

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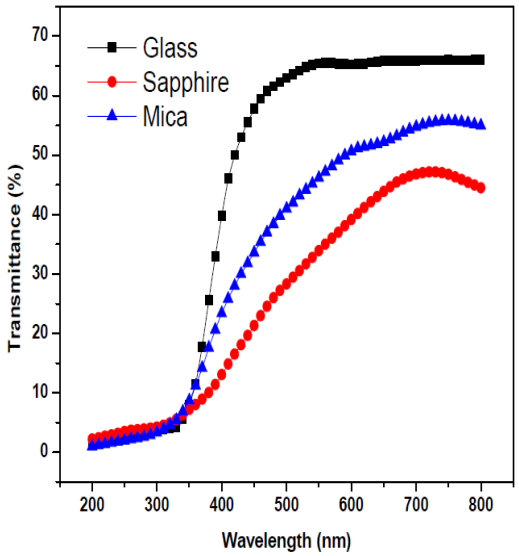
Fig.3.EDAX plot for CuCrO2 thin films deposited on different substrates (a) Glass(b) Sapphire and

(c) Mica respectively.

3.2. Optical properties

Fig. 4 shows the optical transmittance spectra of the CuCrO2 thin films deposited on glass, sapphire and mica. The average transmittance in the visible range is found in all cases and is maximum optical transmittance is obtained for the thin film deposited on glass substrate. The decrease of transmittance in other sapphire and mica substrates may be attributed to the increased scattering of photons by crystal defects created by doping. The increase of optical transmittance of CuCrO2 film on glass substrate can be described to the weakening of scattering and absorption of light because of the defects in the grain boundaries become less. The optical band gap energy calculated using transmittance data is shown in Fig. 5. The Eg is found different in different substrate and is maximum in case of glass substrate as 3.02eV. The observed widening of band gap in case of glass substrate is due to Burstein-Moss effect. The Burstein-Moss effect explained the broadening of band gap energy with the increasing of carrier concentration. It is due to the acceptor hole occupying the states at the top of the valence band.



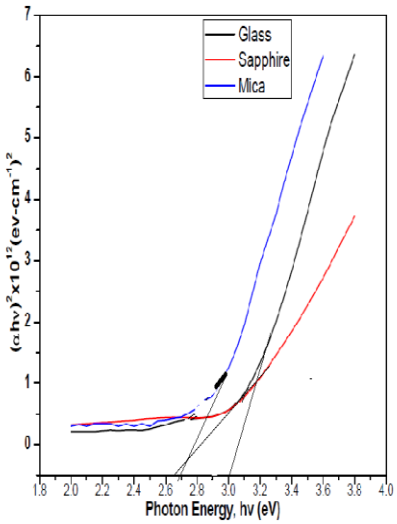


Fig.4.Optical transmittance spectra of CuCrO2 thin films Fig.5.Plot of (αhυ)2 versus photon energy hυ of CuCrO2 thin films deposited on glass, sapphire and mica substrates deposited on different substrates.

These results attributed to the increase of carrier concentration in case of glass substrate. The value of absorption coefficient (α) plays an important role to the limitation of the type of transition. The absorption coefficient values of CuCrO2 films deposited at different substrate materials are found to be ~10^4 cm-1, the value of absorption coefficient decreases with the increase of wavelength. In the shorter wavelengths, the absorption coefficient α exhibits high values which means that there is a large probability of the allowed direct transition, and then α decreases with the increase of wavelength.

3.3.Electrical properties

The resistivity of CuCrO2 thin films deposited on various substrates is shown in Fig.6. The resistivity is found different for different substrates and was minimum in case of sapphire substrate. The resistivity with deposited film on glass, sapphire and mica are 0.994X10-3, 5.442X10-4 and 0.784X10-3 Ω-cm can influence the growth of average grain size, thereby reducing the grain boundary scattering. The variation of resistivity with substrate is also due to the enhancement of film crystallinity, carrier concentration and carrier mobility. The higher the crystal orientation the lower will be resistivity.

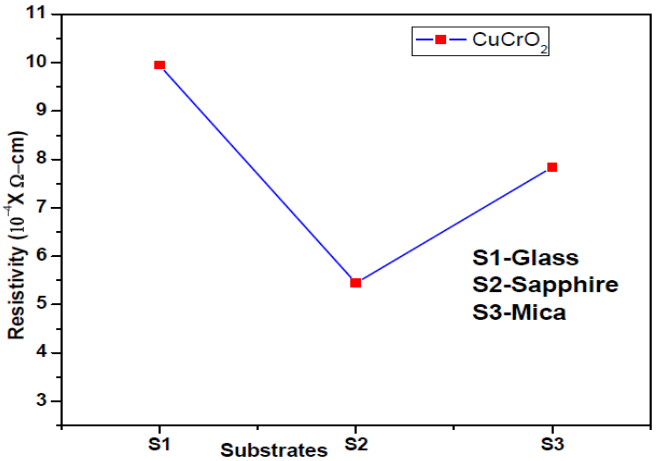


Fig.6 Variation of resistivity of CuCrO2 films with different substrates glass, sapphire and mica

The temperature dependence of electrical conductivity of CuCrO2 thin films deposited on glass, sapphire and mica substrates are shown in Fig.7. It is seen from the plots that for different substrate films have different conductivity and is a linear function of the reciprocal temperature, increases with increasing temperature. Linearity of the plot is nearly the same for all the films. The increase in conductivity with the increase in temperature is due to increasing drift mobility of the charge carriers or due to the lattice vibrations associated with increasing temperature, where the atoms occasionally come close enough for the transfer of charge carriers and conduction is induced by lattice vibrations.

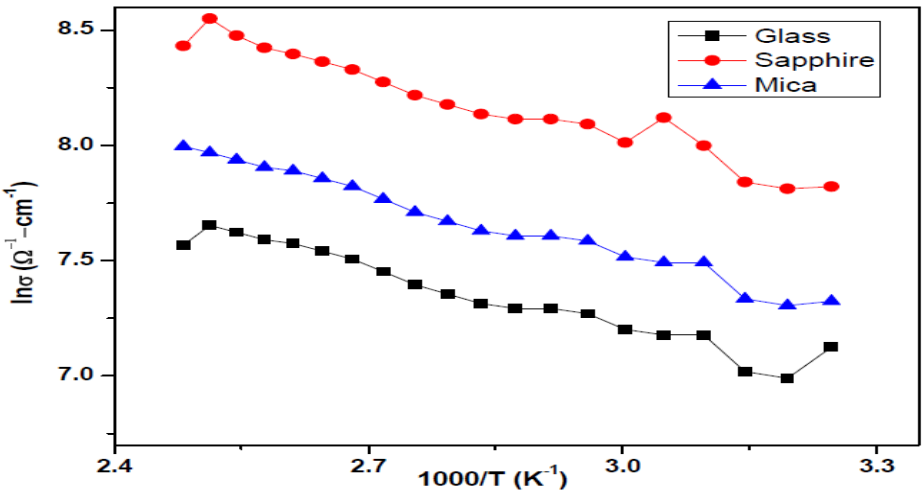


Fig.7. Variation of ln σ versus 1000/T (K-1) for CuCrO2 films deposited on different substrates glass, sapphire and mica.

Variation of mobility of deposited CuCrO2 films on substrates glass, sapphire and mica is shown in Fig. 8. The mobility of the films deposited on glass, sapphire and mica is 46.23, 53.41 and 50.16 cm2V-1sec-1 respectively. The mobility is mainly influenced by grain boundary scattering, lattice defects and impurity by Cr dopants. The mobility vary with the substrate material may be due to the improvement in the grain size and hence decrease in grain boundary, which minimizes the scattering of charge carriers at the grain boundaries.

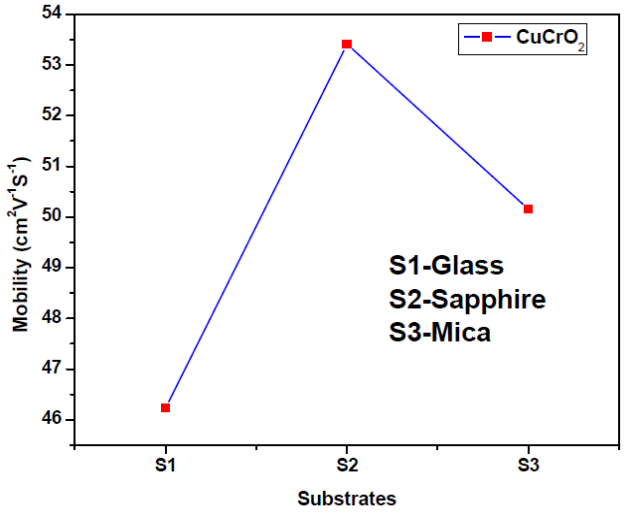


Fig.8.Variation of mobility of CuCrO2 films at different substrates

4. Conclusions

The structural, optical and electrical properties of thin films deposited on various substrates were studied. The substrate is very important for the growth of thin film in terms of lattice and thermal mismatching between substrate and film. In present investigation the structural properties of CuCrO2 films deposited on glass, sapphire and mica were studied from XRD patterns reveled that all the films show the (0 1 2) prominent reflection peak of CuCrO2 with vertical to c-axis as delafossite structure. The diffracted peaks clearly indicated the crystalline nature of the films with diffraction angle 36.78^0, 36.84^0 and 36.74^0respectively. The average crystallite size estimated from Scherrer formula is found 33.05, 36.63 and 34.64 nm for the film of substrates glass, sapphire and mica respectively. The compressive residual strain is found different for different substrate from FESEM images of CuCrO2 thin films deposited on glass, sapphire and mica substrate and revealed that the grains are good adherence with the all substrates and well agglomerated. EDAX plot of CuCrO2 films prepared for different substrates are the evidence from the figure that all the deposition substrates had a significant influence on the stoichiometry of the films. The deviation of stoichiometry is found in all the substrates might be due to the thermal mismatching of surface of substrate. The band gap is found different in different substrate and is high in case of glass substrate as 3.02eV. The variation of refractive index of the films grown on glass, sapphire and mica as a function of wavelength and is high in case of glass substrate.The electrical measurements sugest the conductive behavior is semiconductor in all the substrate films. The films deposited on Saphire has high conductivity reveal that conductivity depends on crystal size and substrate type.

5. ACKNOLEDGMENT

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