Magnetic, Optical and I-V Characteristics of MoO₃ thin films

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Abstract: Molybdenum trioxide (MoO₃) thin films with cobalt concentration were grown on quartz and n-type Si (100) by thermal evaporation deposition technique. Then the films were thermally annealed for 2 hours under normal environment. The structure is analyzed by X-Ray Diffraction (XRD) to confirm the orthorhombic α-MoO₃ phase confirming the crystallinity of thin films. Furthermore, the morphological study is done by Scanning Electron Microscope (SEM) to confirm granular shaped interconnected films. Thicknesses of films are determined by Ellipsometry which vary from 40nm to 140nm with the decrease in Cobalt concentration of thin films. Modifications in optical properties due to the doping of Cobalt in MoO₃ thin films are studied in terms of transmittance data and Taucs plot. All films represent direct band gap transitions. The band-gap of MoO₃ comes out be 3.32eV from the Taucs plot. A slight change in the band-gaps is found for various films with different concentration. Vibrating Sample Magnetometer (VSM) results studied at the room temperature confirm the introduced magnetic property as well as the hysteresis loop for the Cobalt doped MoO₃ thin films.

Keywords: MoO₃, Thin film deposition, Thermal evaporation, XRD, SEM, Optical properties, VSM.

1. Introduction

Spintronics is a new technology being developed where spin of the electron is exploited for carrying the information. This technology merges conventional microelectronics with an innovative era ensuring enormous applications at industrial platform. Spintronics plays with the electron spin to evolve the magnetic properties of the materials [1, 2].

Dilute Magnetic Semiconductors DMS is a subsequent generation of Spintronics that combines non-magnetic semi-conductors with some magnetic material [3]. It is basically a system having just one phase where Transition Metal TM ions swap small fraction of non-magnetic semi-conductors. In this way, an appreciative change in the spin dependent property and magnetic property of the overall alloy of semi-conductor material is evidenced [4]. Recently, Oxide dilute magnetic semi-conductors ODMS are being studied and its several distinctive characteristics is being observed in Spintronics devices and Opto-electronic devices. Nowadays, Transition Metal Oxide TMO Molybdenum Trioxide MoO₃ semi-conductor is being studied. The reason of choosing MoO₃ is due to its large number of industrial usesowing to its attractive properties[5]. MoO₃ is a direct and wide gap semiconductor with many electronic, optical and chemical properties. MoO₃ finds several applications in gas sensing devices, transparent and conducting surface coatings, battery electrodes, solid catalyst and MoO₃ thin films also serve as buffer layers in OLEDs and OPVs [6-10].

In the present study, thermally evaporated MoO₃ thin films have been deposited on silicon and quartz. Doping of MoO₃ is done with different elements like Zinc, Cadmium, Tungsten, Tin and Cobalt etc. to improve its properties. Further than many magnetic elements for doping, Cobalt is being...
mixed in MoO$_3$ to improve some important combination of properties like ferromagnetic phase at room temperature, transparency, electrical conductivity and also semi-conducting properties. Thin films of Cobalt doped in MoO$_3$ semiconductor are used in the application of spin devices, opto-magnetic devices and devices like FETs and LEDs based on spin. Defects as well as oxygen vacancies in MoO$_3$ have a great impact on its properties. Oxygen vacancies favor ferromagnetic ordering by trapping the electrons. These unpaired electron causes ferromagnetism in MoO$_3$. Oxygen vacancies depend on annealing environment. In this present study, air atmosphere is provided for annealing. For applications in spintronics as well as opto-magnetic devices, MoO$_3$ is required to be doped with different magnetic elements like Cobalt to achieve ferromagnetic properties at room temperature and semi-conducting properties. Controlling the injection of spins with proper transfer and their detection helps to attain certain new functionalities and devices like spin FETs and spin-LEDs. The doping of Cobalt in MoO$_3$ improves few properties like optical, magnetic and electrical properties that aids in certain amazing devices applications.

A study has been done to analyze various properties by different characterization techniques [11, 12].

2. Experimental details

2.1 Fabrication of MoO$_3$ thin films by thermal evaporation

MoO$_3$ thin films were deposited on the quartz and n-type Si substrates using the thermal evaporation technique (Hind HivacVacuum Coating (Manual) Model - 12A4D). Both of the substrates were kept 1×1 cm$^2$ in size. First of all, the substrates were cleaned with acetone, trichloroethylene, ethanol and DI water sequentially in the ultra-sonicator. Then they were heated on hot plate to remove any kind of moisture content or water molecule. In thermal evaporation, MoO$_3$ powder were placed in the Mo boats and at a vacuum of 4 × 10$^{-5}$ mbar, the powder was evaporated to get deposited on the substrates placed at a distance above the Mo boat. The deposition was done for 05 minutes. This deposition time was optimized earlier to get thin films of MoO$_3$ below 200nm thickness. For Co doping, various concentrations of Co powder (4%, 6% and 10%) were mixed thoroughly with the MoO$_3$ powder and then thermally evaporated in Mo boats following the same process given above. Thin films obtained after the deposition were amorphous in nature. To make them crystalline, thermal annealing of the samples were done at 500$^\circ$C for 02 hours at room temperature. It is done for 02 hours to minimize the defects and vacancies present in the MoO$_3$ semiconductor. For this purpose, a thermal furnace unit (Metrex microprocessor programmable furnace) was used.

2.2 Characterization techniques

The structural properties of the thin film samples were studied by using X-Ray Diffraction technique XRD (RigakuSmartlab) with a monochromatic radiation of Cu K$_\alpha$ having $\lambda$ of 1.54Å. The surface morphology of the thin film samples were studied by Scanning Electron Microscope SEM (ZEISS EVO Series Scanning Electron Microscope Model EVO15). Thickness measurement and the optical properties were studied by using Ellipsometry technique VASE (Ellipsometer - J A Wollam co. Inc. V-VASE Ellipsometer& VB-400 Ellipsometer control module). The magnetic properties of the thin film samples at the room temperature were done using Vibrating Sample Magnetometer VSM (Versa Lab Free VL096Quantum Design).

3. Results and Discussion

3.1 Structural Analysis by XRD

The structural properties of the thin film samples were analyzed for Co (4%, 6% and 10%) on quartz substrates and n-Si substrates are shown in the Fig.1. It can be seen from the graphs that the films deposited were crystalline in nature. All samples are of annealed thin films. Thin films are sharply defined with orientations in the direction of (020), (040) and (060). These hkl values correspond to the orthorhombic structure of $\alpha$-MoO$_3$ thin films and can be verified as per the JCPDS no. 76-1003 card. The growth of the thin films is found preferably in one direction as can be seen from the hkl values of the peaks from the graph [14].
Fig. 1(a)                       Fig. 1(b)

Fig.1 XRD data for MoO$_3$ thin films and films doped with different concentration of Co (4%, 6% and 10%) on (a) n-Si substrate and (b) quartz substrate

In the XRD graph, it can be noted that there is no peak of cobalt oxide. This proves the low Co doping concentration in thin films of MoO$_3$ that furthermore confirms the substituting doping phenomenon of thin film deposition. Moreover, the orthorhombic form of $\alpha$-MoO$_3$ is also not disturbed in this doping process.

3.2 Morphological Studies by SEM
Fig.2 shows the SEM data for thin films of (a) MoO$_3$ and (b) Co (4%) doped MoO$_3$ on the quartz substrates and silicon substrates. In quartz, it clearly shows the large grain sizes that are forming to establish the crystalline nature of the MoO$_3$ thin films as well as the doped thin films. With the increasing cobalt concentration in the MoO$_3$ thin films, the grain size increases. The morphology of the MoO$_3$ thin films for 4% Co concentration shows continuity in the film and the growth has occurred in the form of round granules that are increasing in size with the doping concentration. In silicon, the shape of the grains also gets changed. The grains are found in the long cylindrical shape. The morphology is of rod shaped which is entirely different form the round shaped granules on the thin films of quartz substrates. So, it can be well said that cobalt doping concentration affirmatively changes the morphological characteristics of the thin films [15].
Table 1 presents the thickness of MoO$_3$ thin films and films doped with various concentration of Co element on quartz as well as silicon substrates. These thicknesses vary from 40nm to 140nm for quartz substrate and 150 nm to 255 nm for silicon substrates as the Co doping concentration is varied. As the Co concentration in MoO$_3$ is kept on increasing, thickness of the thin films moves on decreasing. The melting temperature of Co is much more than the MoO$_3$. On increasing its concentration and keeping the deposition time constant, we get a noticeable decrease in the thickness of the films.

### Table 1 Thickness of various doped thin films of MoO$_3$ on quartz and silicon substrates

| Thin films of          | Thickness (nm) on Quartz | Thickness (nm) on Silicon |
|------------------------|--------------------------|----------------------------|
| MoO$_3$                | 134 ± 0.01               | 255 ± 0.01                 |
| MoO$_3$ + Co (4%)      | 89 ± 0.01                | 198 ± 0.01                 |
| MoO$_3$ + Co (6%)      | 57 ± 0.01                | 160 ± 0.01                 |
| MoO$_3$ + Co (10%)     | 44 ± 0.01                | 149 ± 0.01                 |

3.3 Optical data and studies of thin film samples

Fig.3 demonstrates the transmittance and absorbance graph of MoO$_3$ thin films and Co (4%, 6% and 10%) doped films on quartz substrate. The spectra are recorded for the wavelengths in the visible range from 300nm to 1000nm. The shown spectra of optical transmission for Co (4%) doped thin films display better than 90% optical transparency. Then the Co(6%) doped films show more than 80% transparency. As compared to these thin films, Co (10%) doped and without doped MoO$_3$ thin films show mediocre transparency, still higher than 65%.
Fig. 3 (a) Transmittance and (b) Absorbance data for MoO$_3$ thin films and films doped with different concentration of Co (4%, 6% and 10%) on quartz substrate.

The relationship between the absorption coefficient and the energy of the incident light can be given from the solid band theory and is given by

$$\alpha h\nu = A(h\nu - E_g)^n$$

Here, $\alpha$ = absorption coefficient for various thin films and can be estimated by

$$\alpha = \frac{1}{d} \ln \left( \frac{1 - R^2}{T} \right)$$

$A$ = probability parameter for the transition and is a constant

$E$ = optical band gap energy

$n = 2$ for allowed direct transitions and $\frac{1}{2}$ for indirect allowed transitions.

Fig. 4 displays how $(\alpha h\nu)^2$ is dependent on the photon energy, recalling MoO$_3$ having direct band gap transitions.

Fig.4 Graph of $(\alpha h\nu)^2$ in units of (eV$^2$ m$^{-2}$) set against photon energy of thin films with and without Co doping.

The values of energy band gaps $E_g$ can be estimated by the intersection of the extrapolating straight part of the $(\alpha h\nu)^2$ curves to the $\alpha=0$ ie. zero absorption coefficient. [16]
The calculated optical band gap values are given in the Table 1. It is clearly understood that the various Co doping concentration in the MoO$_3$ films demonstrate no correlation with their band gap energy. It can be explained on behalf of the various oxidation numbers of the element Co that causes inhomogeneous substitution of Co in the MoO$_3$ thin films[17].

Table 2 Energy band gap values of various doped thin films deposited on quartz substrate

| Thin films of          | Energy band gap $E_g$(eV) |
|-----------------------|---------------------------|
| MoO$_3$                | 3.32 ± 0.42               |
| MoO$_3$+Co(4%)         | 3.38 ± 0.05               |
| MoO$_3$+Co(6%)         | 3.18 ± 0.03               |
| MoO$_3$+Co(10%)        | 3.35 ± 0.08               |

3.4 Magnetic analysis

The magnetic properties of various thin films of MoO$_3$ with and without Co concentration doped are studied at room temperature. Basically, the hysteresis loops of these thin films called as M-H loops are plotted and shown in the Fig. 5. Fig. 5(a) shows the magnetization data of MoO$_3$ thin film and MoO$_3$ + Co (10%) on quartz substrate while Fig. 5(b) shows the magnetization data of MoO$_3$ thin film and MoO$_3$ + Co (10%) on silicon substrate. Fig. 5(c) shows the magnetism of undoped MoO$_3$ thin films on quartz and silicon substrates. These magnetic moments with respect to the magnetic field curves are demonstrating ferromagnetic pattern.

Fig.5(a) Quartz substrate  
Fig.5(b) Silicon substrate
Fig. 5(c)

Fig. 5 VSM data for MoO$_3$ thin films and thin films with 10% Co doping deposited on (a) quartz and (b) silicon substrates and (c) magnetism of undoped MoO$_3$ on both substrates

The calculated values of Coercivity (Hc), Magnetization (Ms) and Retentivity (Mr) of thin films deposited on both the substrates are given in the Table 2. It is clearly understood that the various Co doping concentration in the MoO$_3$ films demonstrate magnetism in it and it can be clearly interpreted that the Co concentration of 4% has maximum magnetic values. It is the least doping concentration in our study[18, 19].

Table 3: Coercivity (Hc), Magnetization (Ms) and Retentivity (Mr) values of various doped thin films

| Thin films of          | Hc (Oe) | Ms (emu/cc) | Mr (emu/cc) |
|------------------------|---------|-------------|-------------|
| MoO$_3$ / Quartz       | 133     | 9           | 1           |
| MoO$_3$ + Co (10%) / Quartz | 131     | 11          | 2           |
| MoO$_3$ / Silicon      | 187     | 11          | 1           |
| MoO$_3$ + Co (10%) / Silicon | 187     | 13          | 1           |

It is well reported about the MoO$_3$ for being a paramagnetic compound. It has +4 valency of element Mo in its ternary state [20]. In the contrary, Fig. 5(a) displays a ferromagnetic pattern. The explanation for this conduct can be understood in terms of non-stoichiometry arrangement of MoO$_3$ because of oxygen defects in the deposited films. A small percentage content of various impurities fitting (Mo$_{x}$O$_{3x-1}$) form is probable to occur and not to get detected during XRD study. So, these minority phases are supposed to enhance the magnetic property enabling a transition from paramagnetic to ferromagnetic pattern of thin films of MoO$_3$. Coming to the thin films with doped Co concentration, ferromagnetism arrangement could be contributed by both MoO$_3$ compound and Co element. Thereason behind the cause of ferromagnetism in Co doped MoO$_3$ thin films may be explained in terms of exchange interactions. This interaction comes into existence between the extra conduction electrons due to Mo and localized electrons of Co ions. These localized Co electrons make the conduction electrons spin polarized. These spin polarizations of conduction electrons experience an exchange interaction again with the localized electrons of Co ion that are spin polarized. This progression goes on to mark all of the Co ions spin polarized in one direction.[21-23]
Device Fabrication

MoO$_3$ is well known n-type semiconductor. A p-type Si semiconductor is chosen with n-type MoO$_3$ semiconductor to form a p-n junction diode device. A commercially available p type (boron doped) silicon substrate was taken. It has 100 orientation and thickness of 460 ± 20 microns. The samples were cleaned using the same procedure given in the experimental section of this chapter, before MoO$_3$ deposition. A Hind-Hivac thermal Evaporator Unit (Manual) is used for thin film deposition (MoO$_3$). 20 milligram of Molybdenum trioxide [MoO$_3$], 99.5% (metals basis), mesh powder was used to obtain thin film of MoO$_3$. Another film with 4% Co doping is also made with the same process. Schematic diagram of device made of MoO$_3$ and magnetic doped MoO$_3$ thin films is given in the Fig. 6. From the studies done in the paper, we find that MoO$_3$ thin films with 4% Cobalt doping shows best properties. So, for the comparison in I-V characteristics of p-n junction diode, we have chosen MoO$_3$ thin films and MoO$_3$ films with 4% of Cobalt doping. Annealing of MoO$_3$ deposited on p type Si substrate samples is done using the same parameters explained above. Thickness measurement by ellipsometry was done to find the thickness of the films nearly 100 nm.

![Fig. 6 Schematic diagram of device made of MoO$_3$ and magnetic doped MoO$_3$ thin films.](image)

Contact deposition was done at 21.25x10$^{-5}$ mbar using 1.5 Kilo Ampere current for 05 min. Al which has a melting point of 660 °C was used as contact. A small piece of Al wire of 1.5 mm thickness and 99.999% purity was used.

![Fig. 7 I-V characteristics of device made of MoO$_3$ and magnetic doped MoO$_3$ thin films](image)

The DC electrical measurement was measured by ‘I-V Measurement Cascade Micro-tech MPS 150’ using two-probe setup at room temperature. The current flow through the film is measured in micro ampere range for constant voltages from 0 V to 5 V (in the variation of 1 V). Fig. 7 shows the I–V characteristics of MoO$_3$ thin film and as a function of Co 4% doping concentration by weight. From the Fig. 7, the current (I) value increases by a factor of 10 with Co doping to the corresponding voltage. This is in accordance with the literature [24, 25]. MoO$_3$ is an n-type semiconductor with electrons as majority carriers. Co is an element with 4s$^2$ and 3d$^7$ electrons in its outermost shell. When thin films of MoO$_3$ are doped with Co, it is seen that current
increases. The reason may be attributed because of the free electrons provided by the Co to the MoO$_3$ semiconductor. It might be considered that these increases in the free electrons cause such a huge increase in the current.

Conclusion

Spintronics represents a technology where electron’s spin is utilized for the transportation of the information. MoO$_3$ is an example of Dilute Magnetic Semiconductors under the domain of Spintronics. Oxide -DMS have numerous typical characteristics being useful in Spintronics devices and Opto-electronic devices. In this paper, the structural, surface morphological, optical and magnetic properties of MoO$_3$ thin films and various Co doped MoO$_3$ thin films have been studied. These thin films are deposited by thermal evaporation deposition technique. The structural study done by XRD revealed the crystalline nature of films as all (hkl) values orient in one direction. The morphological study done by SEM proved that the surface of the films on quart substrates has uniform round grains. The grain size has increased with the doping concentration. Thin films on the silicon substrates show cylindrical rod shaped morphology. Hence, it is concluded that the shape of the grains depend on the choice of substrate. In the optical studies, Co (4%) doped thin films exhibited optical transparency better than 90%. Furthermore, the band gap study revealed that the various Co doping concentration in the MoO$_3$ films has no correlation with their band gap energy. The magnetic study of the various Co doped MoO$_3$ films proved some magnetism in it and it was clearly interpreted that the Co concentration of 4% has maximum magnetic values. So, it can be concluded that among the doped concentrations of cobalt in MoO$_3$ thin films, the least Co concentration (4%) thin films have better structural, surface morphological, optical and magnetic properties than other doping concentrations. Furthermore, in current–voltage (I–V) characterization, 4% Co doped MoO$_3$ thin film demonstrated a higher conductivity by a factor of 10 as compared to that of undoped thin films. The DC electrical conductivity was measured of devices made by using MoO$_3$ thin films and Co doped MoO$_3$ thin films. I–V characteristic of MoO$_3$ thin film with Co 4% doping is higher by a factor of 10 as compared to that of without doped thin films. We found very interesting optical and magnetic properties of the deposited film on quartz and silicon substrates. Increased electrical conductivity of thin films demonstrates a new direction for novel spin based devices. These thin films can be extensively developed for Spintronics devices and Opto-electronic devices.

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