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RESEARCH ARTICLE

NANOSTRUCTURED MoO_3-TiO_2 BINARY THIN FILMS BY PERFUME ATOMIZER TECHNIQUE FOR ETHONAL GAS SENSING APLLICATIONS

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ABSTRACT

We wish to report the deposition of MoO_3-TiO_2 binary thin films employing an unique, low cost and simplified spray pyrolysis technique or perfume atomizer method. The MoO_3-TiO_2 binary thin films of different concentration in the range of 3-9 at. % were investigated using glass substrates and temperature kept at 400^0c. The effect of substrate, concentration and temperature on structural, optical, photoluminescence, morphological and gas sensing properties of the chosen binary films has been reported. Structural analysis, using X-ray diffraction technique, verified the phase of the films and revealed that the films has both amorphous and polycrystalline with tetrahedral structure and scanning electron microscope (SEM) measurement showed surface morphology of films changes with increase in concentration. The optical properties of the films including absorption co-efficient and refractive index were determined from spectroscopy measurements. The photoluminescence measurement of binary films indicates that the films exhibit a bright blue emission at 450 nm.

INTRODUCTION

Numerous technological applications of titanium dioxide (TiO_2) such as photoelectrochemical solar cells, photocatalysis, gas sensors etc [1], have led to a wide and growing interest in recent years. In particular, the oxidation affinity, stability and non-toxicity of TiO_2 have intensified the research on environmental applications like dielectrics in memory cell capacitors, semiconducting field effect transistors, antireflective coatings, multilayer coatings and optical wave guides etc., [2-3]. Also, as the titanium oxides are semiconductors with large band gaps, have in depth role in developing various environment and energy related applications. Further, the TiO_2 materials, in general, do have appreciable thermal and chemical stability, good mechanical hardness, and good UV photo activity, excellent transparent to visible light and high refractive index. Henceforth, these materials are found to be suitable candidate for the development of various optical thin film applications [4]. In recent past, many researchers have investigated the possibility of enhancing the properties of TiO_2 when doped with certain transition metal ions like F, Mo, Sb, V, W, etc., [5-14] to a larger extent. In recent years, the fabrication of semiconductors has received more attention due to their extra-ordinary optical and electrical properties and a few luminescent materials have acquired much demand owing to its potential applications in various light emitting devices and communication systems. Nanometer scale materials seem to be proven to be promising candidate for this purpose as they can offer higher luminescent efficiency. Compounds including ZnO, SiO_2, Ta_2O_5, Gd_2O_3 etc., have been reported for their efficient photoluminescent properties [15]. As far as, we aware there are only few reports in literature about the study of photoluminescent properties of TiO_2 and MoO_3 structures and none using a simplified spray pyrolysis technique which employs a perfume atomizer and motivated by the above considerations, we wish to present the results of structural, optical, photoluminescent and morphological properties of MoO_3-TiO_2 thin films synthesized on glass as well as quartz substrates employing a simplified and cost-effective spray pyrolysis technique [16]. To the best of our knowledge binary MoO_3-TiO_2 thin films have not yet been reported. Among various metal oxides MoO_3-TiO_2 thin films have attracted researchers due to their potential applications in the field of solar cells and gas sensors [17-19]. Ethanol is the most important alcohol owing to its divers applications. It is widely used in food industry brewing process control, medical and clinical applications and bio-medical technological processes. These working on ethanol synthesis have great chances of being victims of respiratory and digestive track cancer. Hence, there is a great demand for monitoring ethanol gas at trace level semiconductor metal-oxide based gas sensors are commonly used for environmental monitoring and industrial applications, due to these advantages such as small dimension, low cost and convenient operation. In recent times, the investigation on n-type metal oxides such as ZnO, In_2O_3 and SnO_2 [20-22], has become popular due to their extensive sensing performance.

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Experimental procedure

MoO_3-TiO_2 binary thin films were prepared by a simplified spray pyrolysis technique using perfume atomizer using glass substrates. The Ti and Mo solutions were prepared by dissolving $TiCl_4$ in 5ml of ethanol and $MoCl_5$ in doubly distilled water. Then the two solutions were mixed together with vigorous stirring and MoO_3-TiO_2 films were deposited on to preheated glass substrates. The temperature during the spray deposition was kept at 400^0 c. The Mo:Ti oxide samples of different cationic ratios are labeled as G1, G2, G3 and G4. The crystal structure of the prepared films was analyzed using X-ray diffraction technique ((Phillips x'pert PRO) using Cukα radiation

(λ=1.5405 Å) in Bragg-Brentano geometry θ/2θ coupled and the chemical composition of titanium, oxygen and molybdenum atoms was evaluated using energy dispersive spectrometer (Horiba Jobin Yvon Flourolog III) equipped with 450 W xenon lamp and Hamatsu R928-28 photomultiplier with a computer attached to the setup. Then, the transmittance spectra in the range of 300-1100 nm of the prepared samples were obtained using UV-Vis-NIR spectrometer (Perkin Elmer). The morphological studies of the samples were performed by scanning electron microscope and Atomic force microscope.

RESULTS AND DISCUSSIONS

X-ray diffraction studies

In this investigation, the effect of concentration on the XRD patterns of MoO_3-TiO_2 films were optimized by x-ray diffraction spectroscopy as shown in Fig 2. According Fig. 2 the deposited films on glass substrates which are labeled as G1, G2, G3 and G4. The sample G1, G2 and G3 has no characteristic peak which confirms that the films had amorphous structure. But, G4 film has two prominent peaks (-1 1 1) and (1 1 0) with $2\theta = 25.6^0$ and 27.30^0, these results are in good agreement with standard diffraction data given in standard JCPDS card (no: 01-072-5817, 01-074-6529). So these findings can be concluded that as the deposited films has both amorphous and polycrystalline nature with tetrahedral crystal structure. As in earlier report [23] the sputtered Mo doped TiO_2 thin films has single peak (1 0 1) anatase phase for TiO_2 crystal structure but Mo phase was not found in that XRD patterns. In this discussion the patterns of MoO_3-TiO_2 films has two different peaks [(1 1 0) and (-1 1 1)] (1 1 0) for rutile phase of TiO_2 crystal structure and (-1 1 1) for MoO_3 structure, this effect may be due to the starting materials, deposition temperature (400^0 c) and doping concentration of the prepared samples. These two phases of MoO_3-TiO_2 thin films yet not be reported in earlier work, as discussed above.

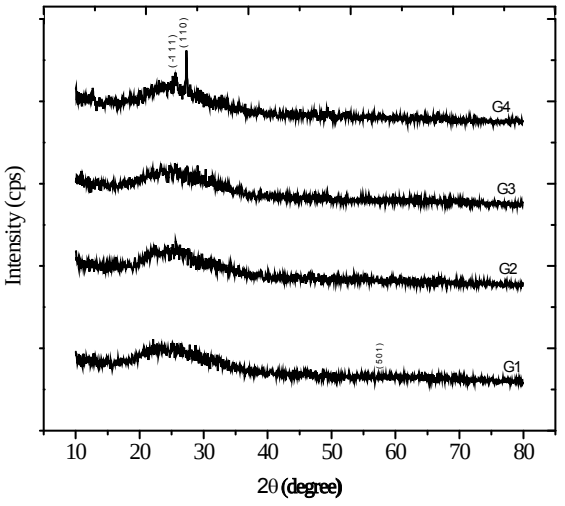


Fig. 1. XRD pattern of MoO_3-TiO_2 binary films

From XRD studies, the grain size was calculated using Full width half maximum (FWHM) of the high intense diffraction peak of both rutile TiO_2 and MoO_3 according to Scherrer formula. The grain size is found to increase for the decrement in FWHM. Also, the thickness of the samples seems to increase, as the average grain size of the MoO_3-TiO_2 thin films was found to increase for prepared sample, which may be due to the more adhesive property of the substrates. However, one could see no change in FWHM as evident in Fig. 2.

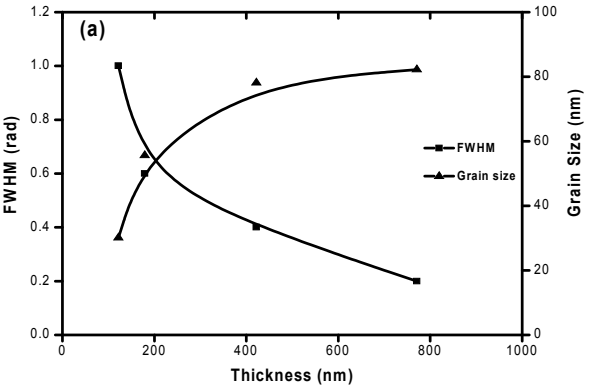


Fig.2. FWHM and grain size of MoO_3-TiO_2 binary films as a function of film thickness

Optical studies

Fig. 3 shows the plot of absorption versus wavelength of MoO_3-TiO_2 binary films deposited with different cationic ratio. The refractive index n and the absorption coefficient (α) of the copper oxide thin films studied here were determined from the transmittance data only using PUMA approach [24]. As seen in Fig. 3, G4 sample has high absorption coeffiecient because of their lower transmissions. Fig. 4 illustrates the dependence of refractive index (n) on the wavelength for different cationic ratio of MoO_3-TiO_2 binary films. It is clear that the refractive index (n) increases with the increase of the higher concentration of deposited films. The refractive index was related to the density and the polarizability of a given material. Thus the changing the concentration of the deposited films could change the density and/or the polarizability of the MoO_3-TiO_2 binary films. Further, the increase of refractive index with concentration may be attributed to an increase in the density of films deposited on heated substrates. Substrate heating provides thermal energy that increases the mobility of the atoms of the films, thereby increasing the packing density of the films [25]. On the other hand, the low value of the refractive index for the MoO_3-TiO_2 binary films indicated that these films had relatively low packing density. Lowering of the packing density is caused by the incorporation of oxygen during film growth [26], which may create voids that absorbs moisture [27]. Moreover, collisions of the evaporated species with O_2 molecules reduce their kinetic energy before reaching the substrate, and this will result in lower packing density.

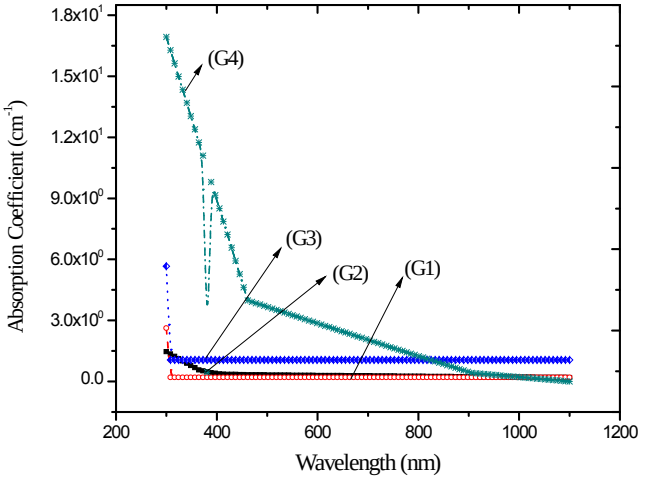


Fig.3. Absorption coefficient of MoO_3-TiO_2 binary films

Fig. 3 shows the absorption coefficient of the MoO_3-TiO_2 binary films. The linear absorption coefficient (α = A/d; where A is the absorbance and d is the thickness of the films) spectra of the MoO_3-TiO_2 binary thin films are shown in Fig. 3. As can be seen in Fig. 3, especially G1, G2 and G3 films have low absorption coefficient at high wavelengths as compared to the other films. We think that, which may be a result of their high transmission values. Besides, it was seen from Fig. 3 that the absorbance decreases with in increases in wavelength range of 400-1100 nm for G1, G2 and G3 sample. But, G4 sample have high absorption co-efficient value attain at 300 nm. So, it was concluded that the fundamental absorption region of G4 films shifts to the higher wavelength. Besides, not all the films have very sharp absorption edges. This indicates that these films have low crystallinity level. So, it was concluded that all films contain high defect density near the band edge [31].

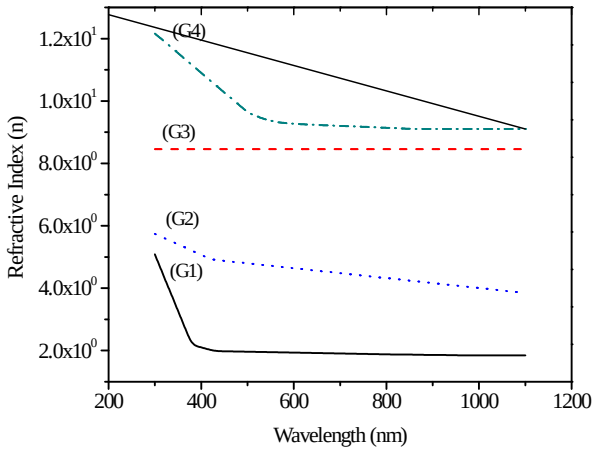


Fig. 4. Refractive index of MoO_3-TiO_2 binary films

Photoluminescence studies

In order to investigate the PL emission spectra of the MoO_3-TiO_2 binary films. Fig. 5 shows that the PL emission spectra of binary films. In Fig. 5, the first three samples show low intensity emission spectra, this may be due to the following aspects: (i) substrate (ii) deposition temperature (400^0 c) (iii) low crystalline clouds on the surface of glass substrate (as confirmed from the XRD studies prepared films). So PL emission spectra of those samples have two intense peaks and broad band centered at 450 nm. The PL emission of MoO_3-TiO_2 films using glass have been interrupted as emission of self trapped excitons and free excitons respectively [28]. These results are concluded that the PL wavelength and PL intensity of prepared films depend on its particle size, crystal structure and deposition temperature. As shown in Fig.5, the three samples has weak intensity peaks, which may be due to the PL spectrum of MoO_3-TiO_2 films could be attributed to the radiative recombination process of self trapped excitations, from the charge transfer excited state of the high dispersed titanium (Ti^{4+}) and molybdenum (Mo^{5+}) species. Therefore, a decrease in PL intensity indicates a weak radiative recombination process. These results are useful for development of advanced optoelectronic, nano devices and optical gas sensor devices based on the wide band gap luminescent metal oxides like MoO_3-TiO_2 films [15]. SEM gives interesting results as shown in Fig. 6 some new information can be obtained from the SEM photographs of the prepared samples. SEM images of MoO_3-TiO_2 films on to glass substrates show that the films were formed as a multilayer net as well as smaller spherical shape with entwined structure, threads aggregated on surface of the films for all glass coated films as shown in Fig. 6, in particular, it is the presence of the nucleating center, such centers initiate the crystal growth, especially in their close neighbourhood. This open and porous nature of the films renders them suitable for gas sensing applications [29].

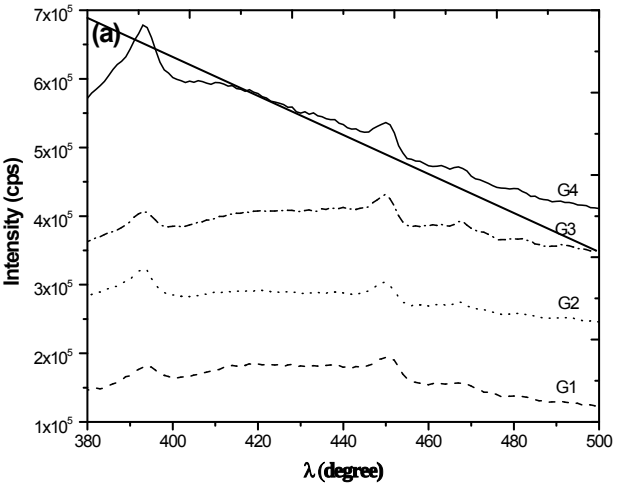
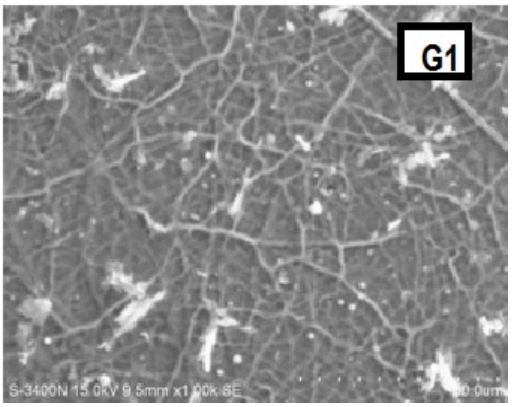
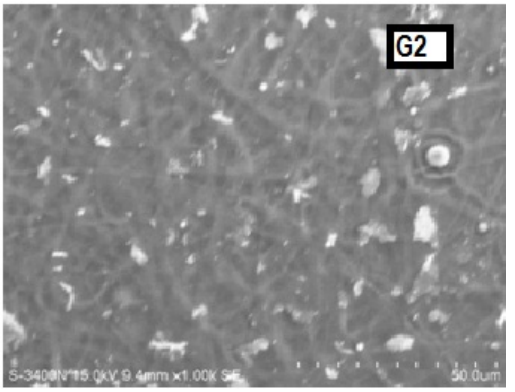
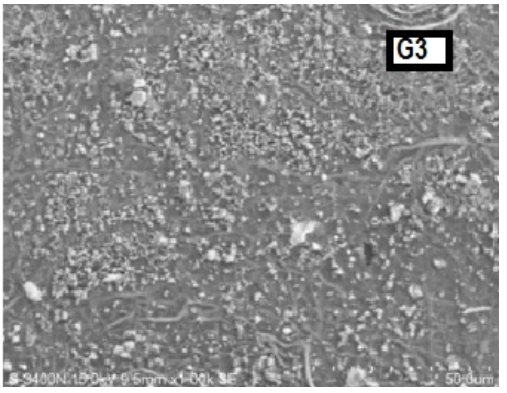


Fig.5. Photoluminescence spectra of MoO_3-TiO_2 binary films on

3.4. Morphological studies







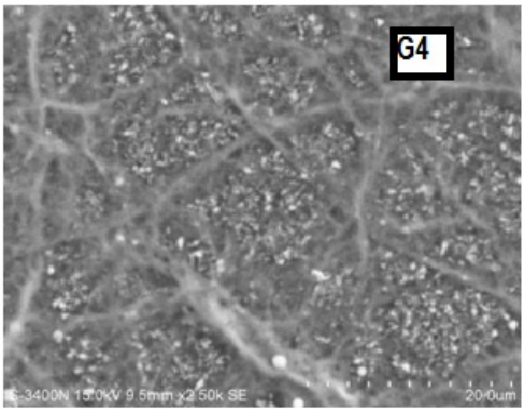
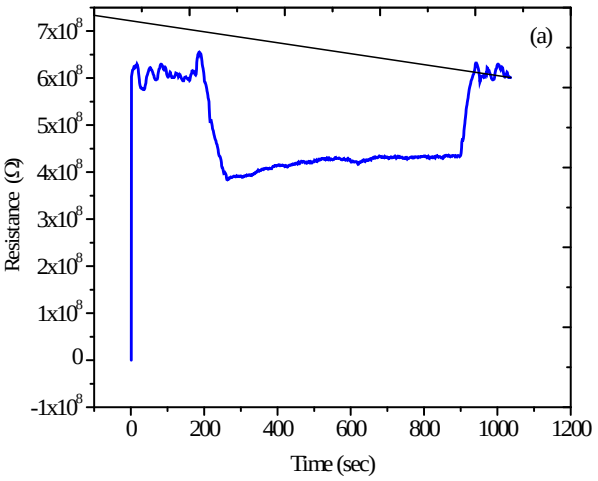
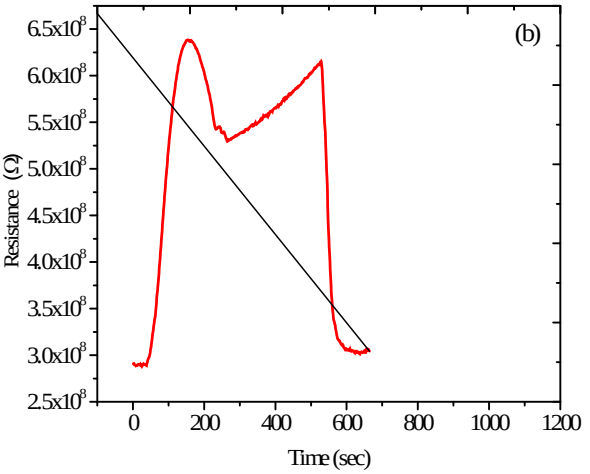


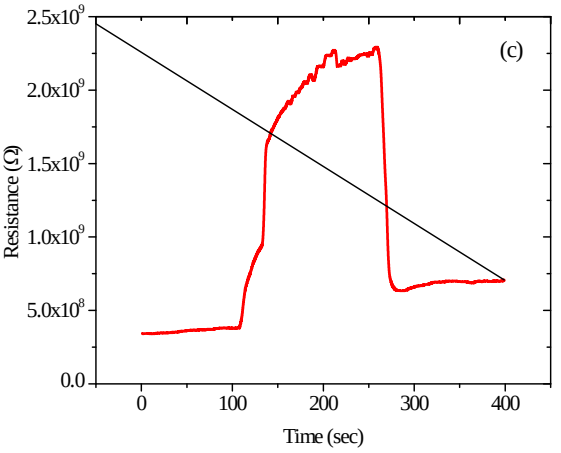
Fig.6. SEM Pictures of MoO_3-TiO_2 binary thin films

Variation in response time and sensitivity of MoO_3-TiO_2 binary thin film sensor

The sensing performance was carried out time versus ethanol gas concentration are presented in Fig. 7(a-d) for MoO_3-TiO_2 binary films. The dynamical resistance of 3, 5, 7 and 9at. % MoO_3-TiO_2 films sensor are respectively with time for 100 ppm of ethanol. Upon exposure to ethanol vapour, the resistance of the sensor decreased upto 220s as seen in Fig. 7(a). The reason for decrease in resistance may be due to the oxidation of the ethanol vapours upon coming in contact with the oxide semi- conducting surface, which liberates free electrons and H_2O. The atmospheric oxygen chemisorbs on the surface of the oxide semiconductor as O^2 or O^-, removing an electron from the conduction band of the semi-conductor [30]. The resistance of the MoO_3-TiO_2 binary films was 3.9 MΩ, 5.5 MΩ, 4 MΩ and 3.5 MΩ for the film prepared different cationic ratio, after exposure of ethanol the films deposited at 9 at. % doping level has resistance 3.5 MΩ. It was also observed that the sensor shows much lower resistance for G4 films (9 at. %) as shown in Fig. 7(d), and a response time of ethanol 51 s, indicating that as the grain size increased with, the MoO_3-TiO_2 binary films sensor shows higher response, therefore the behavior of MoO_3-TiO_2 binary films based sensor to ethanol is based no changes in electrical resistance induced by adsorption or desorption of the gas on its surface [31]. Thus the G4 sample MoO_3-TiO_2 binary films sensor which possesses well define micro structure with uniform grains size, revealed large gas response compare to G1, G2 and G3 sample.







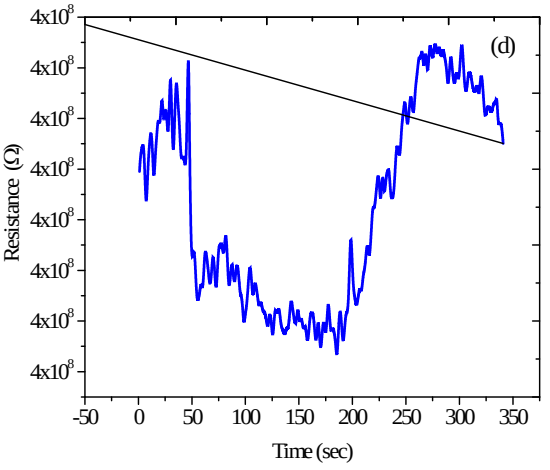


Fig. 7. Response and recovery of MoO_3-TiO_2 binary films

The dependence of sensitivity of MoO_3-TiO_2 binary films on the various concentration is shown in Fig. 8. It is observed that the sensitivity increases linearly as increase concentration from 3 at. % - 9 at. %. The linear relationship between the sensitivity and concentration, the low sensititvity may be attributed to the availability of sufficient number of sensing sites on the films to act upon the lower concentration. The low concentration implies a lower surface

coverage of gas molecules, resulting into lower surface reaction between the surface adsorbed oxygen species and the gas molecules. The increase in the concentration, the surface reaction due to a large surface coverage. Further, increase in the surface reaction will be gradual, when saturation of the surface coverage of gas molecules is reached. Thus, the maximum sensitivity was obtained at 9 at. % for the exposure at 100 ppm of ethanol. The MoO_3-TiO_2 binary films was able to detect upto 100 ppm for ethanol with responsible sensitivity at various concentration. The linearity of the sensitivity with concentration suggested that the MoO_3-TiO_2 binary films can be reliably used to monitor the ethanol gas over in this range.

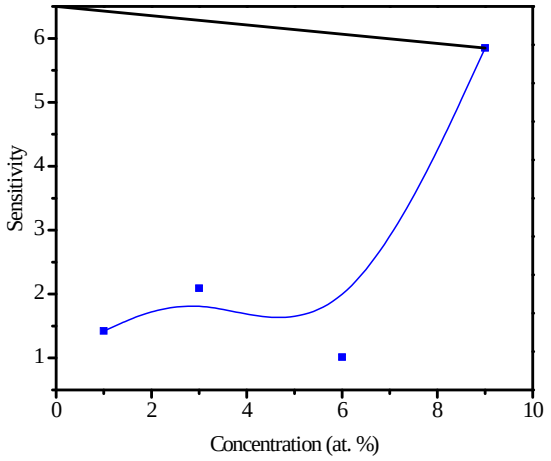


Fig. 8. Variation in sensitivity with various concentration of MoO_3-TiO_2 binary films, towards 100 ppm of ethanol

Conclusion

In the present work, the binary films of MoO_3-TiO_2 have been controllably synthesized by perfume atomizer using simplified spray pyrolysis technique on two substrates (glass and quartz). The XRD studies confirm the formation of rutile Titanium and Molybdenum Oxides thin films. SEM images reveal the improvement of net and flower like structure of binary films for various concentrations. AFM pictures show the porous polycrystalline nature of the samples G4, which suites much for gas sensing applications. A Blue shift of observation edge is observed for the films which may be due to the effect of band bending at the grain surface. Efficient photoluminescence emission observed in all the films can be attributed to high surface roughness exhibited by these films. Moreover, the binary films exhibit a PL emission property in the UV region at room temperature and it is useful in optoelectronic devices and applications, in the future.

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