Gas sensing properties of te thin films: thickness and uv

Thickness and UV irradiation effects on the gas sensing properties of Te thin films

Abstract

In this research, tellurium thin films were investigated for use as hydrogen sulfide gas sensors. To this end, a tellurium thin film has been deposited on Al_2o_3 substrates by thermal evaporation, and the influence of thickness on the sensitivity of the tellurium thin film for measuring H_2S gas is studied. X-ray diffraction (XRD) analysis, scanning electron microscope(SEM) and Raman Spectrometer were utilized for characterizing the prepared samples. XRD patterns indicate that as the thickness increases, the crystallization improves. Observing the images obtained by SEM, it is seen that the grain size increases as the thickness increases, and consequently, fewer defects will be seen in the surface of the film. Studying the effect of thickness on H_2S gas measurement, it became obvious that as the thickness increases, the sensitivity decreases and the response and recovery time increases. Studying the thermal influence of the thin film while measuring H_2S gas, it becomes obvious that as the detection temperature of the thin film increases, sensitivity and the response and recovery times reduce. To improve the response and recovery time of the tellurium thin film for measuring H_2S gas, the influence of UV radiation while measuring H_2S gas was also investigated. The results indicate that the response and recovery times strongly decrease using UV radiation.

Introduction

Tellurium is a P type semiconductor with narrow band gap and a gap energy of 0. 35eV which makes it ideal for use in thin film transistors [1], gas sensors [2-4], optical information storage [5] and shields in passive radiative cooling [6]. Recently, it has been shown that the tellurium thin film is sensitive to some toxic gases like H_2S [7]. Hydrogen sulfide is a toxic and corrosive gas which is formed in coal mines, oil and gas industries, chemical products plants, and the sewers. Exposure to small amounts of this gas (less 50 ppm) causes headache, poor memory, loss of appetite and irritability, while exposure to large amounts (most of 500 ppm) will cause death after 30-60 minutes [8]. So far, various semiconductor metal oxides have been produced for detecting H_2S gas such as SnO_2, WO_3, and CeO_2 [9-11]. The main problem of these sensors is that they require high temperature for measuring H_2S gas, and this high temperature will shorten the life of the sensor[12]. Measuring gas through semiconductor metal oxide depends upon parameters like thickness of the thin film, deposition temperature, and the substrate material. So far, few reports have been issued about the sensitivity of the tellurium thin film to some reducing and oxidizing gases such as NO_2, CO, NH_3, and H_2S [4, 7, 13, 14]. In this research, the influence of the thickness of the tellurium thin film on detecting H_2S gas and also the influence of the film temperature and UV radiation while measuring H_2S gas have been studied.

Experiment details

Tellurium thin films with thicknesses of 100, 200, and 300 nm measured by Quartz digital thickness gauge, were deposited on Al_2O_3 substrate by thermal evaporation of pure tellurium in a tungsten crucible. Substrates were cleaned for 30 minutes by alcohol and acetone in ultrasonic bath. The initial pressure of the vacuum chamber and the temperature of substrate while depositing were respectively 3×10^{-5} mbar and 373K. The growth rate of the film and the deposition area were respectively 5nm/s and $100mm^{2}$. Gold electrodes were deposited on the surface of film through thermal evaporation and copper wires were attached to them by silver paste. The microstructure of the films was characterized through X-ray diffraction (XRD). The morphology of the films surface was determined by scanning electron microscope (SEM). Sensor response to various concentration of H_2S gas was studied in a container made of stainless steel with a volume of $250cm^{3}$. The electrical resistance of the sensors was measured by a multimeter as a function of time. Gas limit detection was performed for the films with different thicknesses and at different environment temperatures. The sensors were also exposed to UV radiation while detecting H_2S gas. The mechanism of gas detection was investigated by Raman spectroscopy technique. The spectra were recorded before and after exposure to the gas. Raman spectra of the films were recorded in back scattering geometry with a spectral resolution of 3 cm^{-1}. The 785 nm line of Ar^{+} laser was used for excitation.

Results and Discussion

XRD patterns of tellurium films with different thicknesses are shown in fig. 1. In this figure, the peaks denoted with star are related to Al_2O_3 substrate. At 100 nm, Te thickness peak of low intensity is observed at 27. 77 ° which is related to Te (101) with hexagonal structure. At 200 nm, in addition to Te (101), another peak corresponding to Te (100) appears at 23. 15 °. Finally, besides Te (100) and Te (101), a new peak is observed at 40. 78 ° which is related to Te (110) with hexagonal structure. From the XRD results, it can be inferred that, thickness increases the results in an increase of film crystallinity due to the increase of the number of planes that generate diffraction. Fig. 2 shows the SEM images of prepared Te films at different thicknesses.[S1]At 100 nm, the grains are separated from each other by a large distance, thereby forming discontinuous and rough surface. Increasing film thickness leads to an increase of surface homogeneity and continuity, grain size increase as well. Fig. 3 depicts the resistance variation of the tellurium thin films with different thicknesses at room temperature before exposure to H_2S gas. It can be seen that the film resistance decrease with thickness increase due to reduction of irregularity in grain arrangement and inhomogeneity on the film surface, which leads to a better charge carrier mobility. The sensitivity of the films to H_2S is given by:

S=

Where R_a and R_g are the electrical resistance of the film in the air and the H_2S respectively. Fig. 4 shows the effect of Te film thickness on sensitivity to 8ppm of H_2S at room temperature. Note that the film sensitivity decreases with an increase in thickness. To explain this behavior, it is worth mentioning that the proposed mechanism for H_2S gas measurement is as follows: the oxygen in the air is adsorbed by the film surface, especially in the grain boundaries and film porosities. After adsorption, oxygen reacts with Te film surface and based on the film temperature, it can be ionized into O_2^-, O^{2-}, O^- (in the temperatures less than 150CËš the ionization form is O_2^-). These forms of oxygen ionization increase the film hole density which means a reduction of R_a in P type semiconductor such as Te. As H_2S gas is added, it reacts with ionized oxygen and the result will be the return of electrons inside the film and reduction of the hole numbers and increase of R_g resistance. The reactions are shown below:

O_2 (gas) O_2 (ads)(1)

O_2 (ads)+ e O_2^- (ads)(2)

H_2S(gas)+O_2^- (ads) H_2 (gas)+SO_2 (gas)+ e(3)

At 100 nm Te thickness, the presence of a high density of grain boundaries and defects results in a high H_2S gas adsorption which causes noticeable variations in film electrical resistance, indicating an increase of sensitivity. At higher thickness, where the grain boundary and defects densities decrease, the changes in resistance are intangible involving a decrease in the sensitivity as shown in fig. 4. The other important characteristic of sensor is its selectivity. The sensitivity on exposure to 10 ppm of CO, NH_3 and NO was found to be 3 %, 40 % and -67 % (negative sign indicates reduction in resistance), respectively[]. Thus we see that the Te films have much larger sensitivity towards H_2S gas in comparison to other gases. Fig. 5 shows the response kinetics of Te films at different thickness (100 nm and 200 nm) after exposure to 8ppm H_2S. Considering the response and recovery times, the times for reaching 90% of steady-state values of R_a and R_g respectively can be defined. It can be clearly seen in fig. 5 that thickness increase leads to an increase of response and recovery times. The former and the latter are due to high adsorption rate of H_2S and O_2 gases, respectively, at 100 nm by the great numbers of grain boundaries and defects [15]. Fig. 6 shows Raman spectra of 100 nm Te sample before and after exposure to 8 ppm H_2S gas at room temperature. In both spectra, peaks at 123, 143 and 267 cm^{-1} are related to tellurium. Two other peaks observed in sample before inducing H_2S gas at 680 and 811 cm^{-1} are assigned to TeO_2 [16]. Notice that the intensity of oxide phase is much less than that of Te phase indicating that a low fraction of Te film is oxidized, which is due to Te atoms on the surface [17]. After exposure to H_2S gas, based on the proposed reaction mechanism the TeO_2 peaks have almost disappeared. In addition, no peak corresponding to H_2S or compounds of sulfur or hydrogen is detected in film after exposure to H_2S gas. Fig. 7 shows the sensors sensitivity as a function of H_2S gas concentration for 100, 200 and 300 nm samples at room temperature. The film to 100 nm Te thickness presents a linear response from the 8 to 34 ppm range and the film sensitivity seems to saturate at higher concentration. As expected, from fig. 7 it can be seen that the sensitivity decreases as the film thickness is increased. Figure 8 shows the results related to response and recovery time for all samples while being exposed to various concentrations of H_2S gas at room temperature. Studying the results it is clear that as the H_2S gas concentration increases, the response time decreases and the recovery time increases. This is because as H_2S gas concentration increases, the probability of a reaction between gas and ionized oxygen becomes more probable, and more reactions will be observed in a shorter time which causes the resistance to change faster and finally reach a constant level. As the concentration goes up, more H_2S gas molecules are absorbed and their desorption requires a longer time. The resistance of different samples as a function of detection temperature before exposure to H_2S gas is shown in fig. 9. In all thickness, a decrease of resistivity is observed with temperature increase due to electrical properties of semiconductor, as well as increase of oxidation reaction rate. In the case of 300 nm Te films the variation of resistance is insignificant because of the very low resistance of this sample. Fig. 10 shows the results related to sensitivity as a function of temperature while being exposed to 8ppm of H_2S gas. Investigating the results, it is found that temperature rise leads to reductions in sensitivity in all samples, because the number of charge carriers in samples increases as the temperature rises and as a result, when samples are exposed to H_2S gas, no tangible resistance change is observed and sensitivity decreases [18]. In samples with 300nm thickness and with temperatures above 90C ° there is no sensitivity against H_2S gas, since the number of charge carriers is so high that their change is never tangible by reaction with H_2S gas. Fig. 11 shows the recovery and response times as a function of temperature while being exposed to 8 ppm H_2S gas. In all samples, as the temperature rises the response and recovery time decreases. Overall, two factors are effective for a reaction: first, the molecules which are going to take part in the reaction must have a lot of energy, second, they must collide with one another in an appropriate direction. Temperature rise causes an increase in energy and more effective collisions will take place between reactants, and the response and recovery time decrease. To study the effect of UV irradiation on the sensor properties during the gas detection, samples are simultaneously exposed to 8 ppm H_2

S gas and UV radiation at room temperature. Fig. 12 shows a comparison between the sensor sensitivity of the UV exposed and unexposed cases as a function of Te film thickness. It is obvious that application of UV radiation results in a dramatic reduction of sensors sensitivity. As it is well-know, UV radiation creates supplementary charge carriers by an excess of electron-hole pairs formation. Increase of charge carriers number involves a decrease of resistance such that the changes of resistance are not tangible while reacting with H_2S gas. Fig. 13 presents the recovery and response times as a function of H_2S gas concentration before and after exposure to UV radiation. It is observed that the recovery and response times strongly depend on UV radiation. These two parameters decrease with UV radiation due to creation of electron-hole pairs. The created electrons react with adsorbed oxygen, so the number of ionized oxygen reacting with H_2S gas increase, which can result in an increase of reaction rate between oxygen and H_2S gas. The above explanations can be summarized in the following reactions:

O_2 (gas) O_2 (ads)(4)

O_2 (ads) + e O_2^- (ads)(5)

hν e + h

O_2^- (ads)+ e 2O^- (ads)(6)

H_2S(gas) + O^- (ads) H_2 (gas) + SO(gas) +e(7)

It is worth noting that the increase of UV radiation intensity has no effect on sensitivity, response and recovery times of Te sensors. Also, to evaluate sensor stability, the samples of 100 nm and 200 nm Te film were subjected to 8 ppm H_2S at room temperature for 60 days, then their basic resistance and sensitivity were measured as shown in fig. 14. The results indicate that both resistance and sensitivity of sensors remain nearly constant, confirming suitability of Te films for use as sensor.

Conclusion

In this work, thickness effect of Te films for H_2S gas sensing are investigated. A strong dependence on electrical resistance and sensitivity to Te film thickness is observed. This means that increasing the thickness leads to a decrease of sensor sensitivity and increase of response and recovery times. Considering the sensing mechanism of Te thin films which is based on the interaction of ionized oxygen with H_2S gas, the grain boundaries and the surface roughness could be considered as active sites for trapping the gas molecules. Thickness increase leads to a decrease of these active sites. The results show that although the Te sensor can operate at room temperature, a decrease of response-recovery times can be obtained at higher operating temperatures. Raman spectroscopy shows that adsorbed oxygen on the surface of Te films can be removed after exposure to H_2S gas, leading to changes in the film resistance, UV radiation, as well as response-recovery times. The prepared sensors present a stability in sensitivity and resistance for 60 days after exposure to H_2S gas which confirms their ability to be used as H_2S gas sensor.