Research Article

Electrical and Optical Properties of $\text{Ge}_x\text{Si}_{1-x}:\text{H}$ Thin Films Prepared by Thermal Evaporation Method

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Thin a- $\text{Ge}_x\text{Si}_{1-x}:\text{H}$ films were grown successfully by fabrication of designated ingot followed by evaporation onto glass slides. A range of growth conditions, Ge contents, dopant concentration (Al and As), and substrate temperature, were employed. Stoichiometry of the thin films composition was confirmed using standard surface techniques. The structure of all films was amorphous. Film composition and deposition parameters were investigated for their bearing on film electrical and optical properties. More than one transport mechanism is indicated. It was observed that increasing substrate temperature, Ge contents, and dopant concentration lead to a decrease in the optical energy gap of those films. The role of the deposition conditions on values of the optical constants was determined. Accordingly, models of the density of states for the $\text{Ge}_{0.5}\text{Si}_{0.5}:\text{H}$ thin films as pure, doped with 3.5% of Al (p-type) and that doped with 3.5% As (n-type), were proposed.

1. Introduction

Amorphous semiconductor materials have become of more interest in the last three decades because of their physical properties for many applications in the area of optoelectronics, such as the fabrication of solar cells, photoconductors, and other optical devices [1, 2]. One of the interesting compounds in this line is the alloy system of $\text{Ge}_x\text{Si}_{1-x}$. The advantage of this alloy material is the possibility for it to vary its band gap with the germanium concentration x and thus improves its wavelength response [3–5].

Hydrogenation of such films enhances its quality. Previous studies reported that formation of Si–H and Ge–H bonds leads to a considerable reduction in the density of states of thin films and hence better film performance [6–9].

Extensive research on hydrogenated amorphous silicon-germanium (a- $\text{Si}_{1-x}\text{Ge}_x:\text{H}$) films has been carried out using various techniques [4, 5, 10–13] for preparing a competitive material in many applications of optoelectronic devices [14, 15].

In this work, alloys of $\text{Ge}_x\text{Si}_{1-x}$ were prepared and thin a- $\text{Ge}_x\text{Si}_{1-x}:\text{H}$ films were deposited on glass substrate

by thermal evaporation method. The pure material and that doped with Al and As were investigated for their electrical and optical properties. A correlation between the optoelectrical properties and deposited parameters of the films prepared at different value of Ge content in the alloy of $\text{Ge}_x\text{Si}_{1-x}$ was observed. A proposed model for density of states for the pure system $\text{Ge}_{0.5}\text{Si}_{0.5}:\text{H}$ thin film and with doped value of 3.5% of Al and 3.5% As was suggested.

2. Experimental Procedure

Ingots of $\text{Ge}_x\text{Si}_{1-x}$ with $x = 0.3, 0.5$, and 0.7 were prepared in evacuated quartz tubes. Elements of 99.999% purity were used in preparation of the alloys [15]. Amorphous $\text{Ge}_x\text{Si}_{1-x}:\text{H}$ thin films were fabricated using thermal evaporation method. Different deposition conditions were introduced to prepare the films such as substrate temperature and dopant concentration of Al for p-type and As for n-type hydrogenated thin film.

Film thickness of about 350 nm were grown at a deposition rate of 0.9 nm/s while the average vacuum pressure during the deposition was $(1-2) \times 10^{-6}$ Torr. The hydrogenation

took place in situ by exposing the various fabricated system of $\text{Ge}_x\text{Si}_{1-x}$ to hydrogen plasma under an optimum pressure of 0.17 Torr.

The structure and the composition of the prepared films were determined using X-ray diffraction, X-ray fluorescence and energy dispersive spectroscopy. These confirmed the films stoichiometry. The Fourier transform infrared spectroscopy was employed to observe the existence of various vibrational modes in $\text{Ge}_x\text{Si}_{1-x}:\text{H}$ films.

Dark dc conductivity (σ) for prepared a- $\text{Ge}_x\text{Si}_{1-x}:\text{H}$ films was measured as functions of substrate temperatures (T_s) for various value of (x) of the compound.

Optical transmission spectra of the a- $\text{Ge}_x\text{Si}_{1-x}:\text{H}$ films were measured with double-beam Perkin-Elmer Lambda 9 spectrometer within the ranges of (300–2500) nm. The transmission spectra were used to determinate the absorption coefficient (α), the optical energy gap (E_g), and some optical constants of the prepared thin films. Calculated optical constants are the refractive index (n), extinction coefficient (k), and real and imaginary parts of the dielectric constant (ϵ_1 , ϵ_2) of the prepared films using the envelop technique described by Swanepoel [16].

3. Results and Discussion

3.1. Role of Deposition Parameters on the Dark dc Conductivity. The temperature dependence of dc conductivity (σ) was obtained using Stuke's formula [17]:

$$\sigma = \sigma_o \exp\left(-\frac{E_a}{kT}\right), \quad (1)$$

where σ_o is the minimum metallic conductivity, E_a is the activation energy, k is the Boltzmann constant, and T is the absolute temperature.

Figures 1(a)–1(c) exhibit the variation of conductivity with the reciprocal of (kT) in the temperature range between 300 and 503 K for various a- $\text{Ge}_x\text{Si}_{1-x}:\text{H}$, deposited at different substrate temperatures (T_s = room temperature (RT), 373, and 503 K), with different values of x . These data indicate the existence of more than one conduction mechanism throughout the heating temperature range.

The activation energy (E_a) of deposited films was deduced from these data. The result of such calculation and the variation of conductivity at room temperature ($\sigma_{R.T}$) as function of x for film deposited at various substrate temperatures are shown in Figures 2(a) and 2(b). The graph indicates a clear dependence of the activation energy on the substrate temperature, and it decreases slightly with increasing x . The effect of T_s on $\sigma_{R.T}$ becomes clearer for $x > 0.5$, whereas the dark dc conductivity at room temperature ($\sigma_{R.T}$) increases strongly with value of x for three values of substrate temperature (T_s) of the hydrogenated thin film. This may be due to change in the localized states at the band edges of the deposited thin films at higher temperature and the rearrangement of the atoms on the surface of the substrate which lead to films with fewer defect as described by Alias [18]. These illustrations also show that the role of x on the activation energy is manifested better for film deposited at room temperature in comparison with film

deposited at higher substrate temperature. This might be because the atoms deposited at higher substrate temperature possess enough energy end-up in stable state in the structure of the film. The same tendency was observed by other authors [19, 20].

3.2. Effect of Preparation Conditions on the Optical Energy Gap. The optical absorption coefficient (α) was determined from the transmission spectrum of a- $\text{Ge}_x\text{Si}_{1-x}:\text{H}$ thin films prepared under various deposition conditions. The optical energy gaps (E_g) of these films have been obtained through using Tauc formula [17, 21]:

$$\alpha h\nu = B (h\nu - E_g)^r, \quad (2)$$

where B is inversely proportional to the film's amorphousity and $h\nu$ is the incident photon energy. The values of r depend on the electronic transition nature of the deposited films. The best fit of the data determined a value of 2 for the r .

Figures 3 and 4 show the change of optical energy gap (E_g) with film growth parameters (x , doped concentration of Al and As, resp.). From these data one can draw the following observations: E_g decreases with the increase of both Ge content (x) and substrate temperature (T_s) for both types of dopants. This behavior might be due to the creation of new states within the energy gap as the content of Ge rises in the material [19] further, the films deposited at higher substrate temperature could have lower H contents as supposed by Xu et al. [19]. On the other hand films fabricated under such conditions could possess less randomness in their amorphous structures, since better arrangement of the atoms would occur at higher substance temperature, leading to a decrease in the optical energy gaps [17].

The study also indicated a decrease in E_g with the increase of the percentage of the dopant concentration of Al and As. This tendency may be attributed to an elevation in the impurity states within the gap, which causes a shift in Fermi level either toward the valence or conduction band according to the type of the dopant. Such factor could be the main reason for narrowing the optical energy gap for films deposited at higher percentage of the concentration of both types of dopants. Another noticeable observation from Figure 3 is the lower E_g for p-type than that for n-type and pure $\text{Ge}_x\text{Si}_{1-x}:\text{H}$. A similar trend was observed by other researchers [19, 22].

3.3. Effect of Deposition Parameters on the Optical Constants. Figures 5(a) and 5(b) illustrate the variation of refractive index (n) and extinction coefficient (k) with different Ge content (x) for pure and doped a- $\text{Ge}_x\text{Si}_{1-x}:\text{H}$ thin films. Doping was performed at 503 K with 3.5% As and 3.5% Al. The data show that n increases with increasing x for pure and doped thin films. This could result from the increase in the packing density of the films grown with high x since the refractive index for Si is smaller than that for Ge. Also the data highlight an increase in k as x increases for all types of films. This could be due to increase in the absorption

FIGURE 1: Variation of $\ln \sigma$ with reciprocal of (kT) for a-Ge_xSi_{1-x}:H, thin films, deposited at different substrate temperatures: (a) RT, (b) 373 K, and (c) 503 K.

FIGURE 2: Variation of (a) σ_{RT} and (b) E_a as function of Ge content (x) for a-Ge_xSi_{1-x}:H thin films at different substrate temperatures.

FIGURE 3: Variation of E_g as a function of T_s for films deposited with different values x in pure and doped $a\text{-Ge}_x\text{Si}_{1-x}:\text{H}$ thin films with various percentage of Al.

FIGURE 4: Variation of E_g as a function of T_s for films deposited with different values x in pure and doped $a\text{-Ge}_x\text{Si}_{1-x}:\text{H}$ thin films with various percentage of As.

FIGURE 5: Variation of (a) n and (b) k with Ge content for pure and doped (3.5%As and 3.5%Al) for $a\text{-Ge}_x\text{Si}_{1-x}\text{:H}$ films.

FIGURE 6: Variation of (a) ϵ_1 and (b) ϵ_2 with Ge content for pure and doped (3.5%As and 3.5%Al) for $a\text{-Ge}_x\text{Si}_{1-x}\text{:H}$ films.

FIGURE 7: A proposed model of the density of states for (a) pure, (b) p-type, and (c) n-type for a-Ge_{0.5}Si_{0.5}:H thin film.

coefficient and as a conformation of the data shown in Figures 3 and 4 for decreasing the optical energy gap with an increase in the Ge content (x).

Figures 6(a) and 6(b) show the variation of real (ϵ_1) and imaginary (ϵ_2) dielectric constants for pure and doped (3.5% As and 3.5% Al) films deposited at 503 K. It could be derived from these data that the increase in Ge content leads to elevation in the value of both ϵ_1 and ϵ_2 for the three types of thin films.

3.4. Proposed Model for Density of States for Pure and Doped a-Ge_{0.5}Si_{0.5}:H Films. Referring to the data provided above, we suggest a model for the variation of the density of states in the mobility gap. The suggested model is based on a comparison between the values of the dark dc conductivity and the optical energy gap for pure and doped films with 3.5% of As and 3.5% Al. This is shown in Figure 7. Our measurement confirmed that all systems of a-Ge_{0.5}Si_{0.5}:H thin films doped with Al are p-types whereas those doped with As are n-type.

The conductivity activation energy means that the distance between Fermi level with top of the valence or bottom of the conduction bands depends on the type of majority carriers (holes or electron). The following observation can be deduced from the data shown in Figure 7:

- (i) a reduction in the optical edge from 0.87 eV for pure film to 0.77 eV and 0.75 eV for doped a-Ge_{0.5}Si_{0.5}:H thin film with 3.5% As and 3.5% Al, respectively;
- (ii) a shift of Fermi level towards valence band around the value of 0.09 eV for films doped with 3.5% Al, while it is about 0.06 eV toward the conduction band for film doped with 3.5% As;
- (iii) the width of the tail is the same near the edge of the conduction band (E_C) and the edge of the valence band (E_V). That is, $E_C - E_A = E_B - E_V$. The tail width and the density of states variation near Fermi level according to both dopant types and pure film of a-Ge_{0.5}Si_{0.5}:H are highlighted in Figure 7.

4. Conclusion

Thin a-Ge_xSi_{1-x}:H films were grown successfully by fabrication of designated ingot followed by evaporation onto glass slides. Film composition and deposition parameters were investigated for their bearing on film electrical and optical properties. The summary of the study is provided in the following.

The dark conductivity of a-Ge_xSi_{1-x}:H thin film increases with the increase of the substrate temperature, dopant concentration of As and Al, as well as with the Ge contents in the grown systems.

The activation energy decreases with both increasing Ge content (x) and the substrate temperature.

The optical energy gap of the hydrogenated amorphous thin film of Ge_xSi_{1-x} decreases with both substrate temperature and the percentage of dopant concentration for n- and p-types thin films.

Both the refractive index and the extinction coefficient of a-Ge_xSi_{1-x}:H thin films were increased with the value of x . Note that the values of the n and k for p-type are higher than those for n-type and pure film deposited at all substrate temperatures. The same trend of behavior was observed for real and imaginary parts of the dielectric constant.

A model has been deduced from the obtained data for density of states for pure and doped a-Ge_{0.5}Si_{0.5}:H thin film.

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