JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

Structural and optical properties of Ge nanocrystals grown by annealing of Germanium oxide thin films

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Abstract: In this report, we have investigated the evolution of Ge nanocrystals in GeO_2 matrix upon increasing the annealing time at a fixed temperature. The GeO_2 thin films were deposited on Si and Quartz substrates using e-beam evaporation. Afterwards the deposited films were annealed at temperature of 650°C for three different durations. The evolution of Ge nanocrystals has been seen at 650°C which is evident from the Raman spectra while the reduction of nanocrystals after annealing for 90 minutes has been explained. Further, the optical properties were studied using UV-Vis-NIR spectroscopy of GeO_2 thin films. The transmittance is observed to decrease upon increasing the annealing time. The effect of annealing time on the Ge nanocrystals growth in GeO_2 matrix and the optical properties of GeO_2 thin films have been discussed in the present study.

Introduction:

In the present scenario, the word ‘nanomaterials’ has become a point of talk. It is being used in a lot of consumer gadgets and products as a special feature. Many books, articles and journals have been devoted to nanomaterials as it has become a very interesting and useful topic of research in the various fields of Physics and Chemistry.

So, the important question that hits everyone’s mind is that ‘What are nanomaterials?’ The answer to this question is quite specified by the name ‘nanomaterial’ which points towards the nanoscale. So, the materials having size less than 100 nm, at least in one dimension are nanomaterials. Despite having the same compositions, different structural, optical, thermal and electrical properties from their bulk counterpart make the material very special at nanoscale. The reasons behind the change in the properties from bulk to nanoscale is the large surface to volume ratio in the nanomaterials and arise of the ‘quantum confinement’ effect at the nanoscale. The quantum confinement comes into picture when the size of bulk material is reduced below Bohr exciton radius which is defined as the radius of an electrostatically bound electron-hole pair in the bulk material.

According to dimensionality, the nanomaterials are referred as zero dimensional (such as quantum dots), one dimensional (such as nanowires and nanorods), two dimensional (such as nanowalls and nanocoatings) and three dimensional (such as nano powder) nanomaterials. They

are synthesized or prepared by using two different approaches. One is bottom-up approach in which the building blocks are atoms and molecules, and the other is top-down approach. The size dependent properties of nanomaterials have attracted a great attention due to their wide range of applications in various fields such as solar cells, light emitting devices, electronics, optoelectronics, medical and so on.[1]

Germanium (Ge) is a grayish-white metalloid in the carbon group, which is quite similar to silicon and tin (the other group members). In pure form, it is a semiconductor having quite same appearance as that of silicon. Ge is hard-brittle and lustrous.[2] Ge nanocrystals were discovered in 1982 by Hayashi et. al.[3] but they termed them 'microcrystals'. The choice of Ge nanocrystals instead of other materials such as CdS, GaAs and PbS is well supported by its non-toxic nature, bio-compatibility, electrochemical stability and compatibility with current microelectronics. When compared with crystalline silicon (Si), Ge nanocrystals are found to be better than Si because of large electron and hole mobilities, large dielectric constant, smaller energy band gap and larger Bohr exciton radius.[3] Ge exhibits face centered diamond cubic structure, shown in the figure-1. The structure consists of an fcc lattice having a basis of two atoms of Ge. These are situated at (0,0,0) and (1/4,1/4,1/4) in units of cubic edge. Two interpenetrating fcc lattices of Ge atoms having origins displaced by (1/4,1/4,1/4) can give us the best visuals of the crystal structure of Ge.[4]

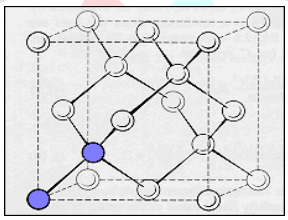

Figure 1: Crystal structures of Ge

Ge is an indirect band gap semiconductor from group 14 with atomic number and atomic weight of 32 and 72.6 u, respectively. The electronic configuration of Ge is [Ar] $3d^{10}$ $4s^2$ $4p^2$. It is solid at STP. The other properties of Ge are as given in the following table 1.[2]

Table 1: Properties of Ge

Property	Value
Atomic radius	1.22 Å
Density	5.33 g/cm^3
Phase at STP	Solid
Melting point	1211.40 K
Boiling point	3106 K

Color	Grayish-white
Crystal structure	Face centered diamond cubic
Lattice constant	5.65 Å
Band gap	0.67 eV
Band gap type	Indirect band gap
Bohr exciton radius	24.3 nm

Ge has been a material of a lot of applications in the area of optoelectronics and microelectronics devices. In the present report, for studying the role of the annealing time on the structural and optical properties of Ge nanocrystals in GeO_2 matrix at a fixed temperature in detail, various characterization techniques have been used.

Method of Deposition and Characterization Techniques:

- **Electron Beam Evaporation:**

The electron beam (e-beam) evaporation is a kind of physical vapor deposition technique in which the target material to be deposited on the substrate, is bombarded by a beam of electrons produced from a tungsten filament in the electron gun. This leads to the evaporation of the target material inside the chamber. Since the whole process is taking place in high vacuum, these atoms or molecules then precipitate on the substrate and a thin film is formed. The e-beam evaporation basically overcomes the difficulties that occur in thermal evaporation, such as when the melting point of target material is high. There is direct transfer of energy of electrons to the target material so that materials of any melting point can be evaporated with it. This makes it ideal for metals with high melting point. The deposition rates are significantly higher (from 0.1 nm/min. to 100 nm/min.) which yields a high density thin film deposited on the substrate surface. Also, since we are concentrating the energy which is transferred through focused e-beam, only on the target material, therefore we can get rid of the contamination from the crucible in which target material is kept and the substrate can also be kept away from the heat damage.

The chamber is evacuated with the help of rotary pump and diffusion pump to create a vacuum of the order of 10^{-6} mbar. The thickness of the thin film is generally monitored by using a quartz crystal. This quartz crystal helps in maintaining the necessary power and evaporation rate. The power of e- beam is swept all over the target material with the help of XY sweeping. Generally, there is no requirement of XY sweeping for the materials having low melting points but for those possess higher melting temperature, XY sweeping is very helpful in maintaining

uniformity of the film. This is due to the fact that the materials with low melting point completely fill the crucible while a hole is created in those having higher melting point by the electron beam. Due to this hole, there will be uneven discharge of coating material over the thin film. For the sake of cooling to prevent the impurities of the crucible in the thin film, water is circulated throughout. The electron beam evaporation is widely used in many fields such as solar panels, laser optics, in eye glass and architectural glasses.[5]

- **Raman spectroscopy:**

Raman spectroscopy is spectroscopic technique which is based upon Raman scattering (a kind of inelastic scattering of photons). Sir CV Raman received the Nobel Prize in 1930 for this work. It is used for studying the rotational, vibrational and other low-frequency modes in molecular gaseous, liquid or solid systems. Since the vibrational spectra of gases, liquids and solids are very sensitive to changes in bond lengths, bond strengths and arrangements of bonds, thus Raman spectrum also responds critically to defects and disorder. The Raman spectroscopy has become a significant fingerprint tool for material identification and analysis.

Raman Effect: When a material is irradiated by electromagnetic (*em*) radiation, the photons interact with the electrons of the molecular system of the material and the electron cloud of the molecule gets distorted leading to the formation of an unstable virtual state for an infinitesimal time. The molecule relaxes into the vibrational state by emitting a photon. It leads to the following cases:

(i) If the molecule is excited from some state to a virtual state and relaxes to the same state, then the frequency of the emitted photon will nearly remain same because the energy shift will be minute due to the small size of the electron. This elastic scattering is known as Rayleigh scattering.

(ii) If the molecule is excited from the ground state vibration level to a virtual state and relaxes to some excited vibrational state, then the re-radiated photon will be shifted to a lower frequency, which is called a Stokes shift.

(iii) If, initially, the molecule is in an excited vibrational state and the molecule relaxes to the ground state vibrational level, then the energy of the emitted photon will be shifted to a higher frequency and this is called the anti-Stokes shift.

This inelastic scattering phenomenon constituting both of the shifted frequencies is known as Raman scattering effect.[6] The scattering of the *em* wave is caused by its interaction with the different molecular vibrational modes of the material. The molecular vibration strengths vary for different types of bond such as single, double or triple bonds.

- **UV-Vis-NIR Spectroscopy:**

UV-Vis-NIR spectroscopy is a spectroscopic technique that gives the quantitative measure of amount of light absorbed and scattered by a material. In this technique, a sample is placed between the incident light and photodetector. The difference between the intensity of the

incident light on the sample and intensity of light that comes out of the sample after absorption and scattering is measured and compared at each wavelength so as to get the spectrum depending on the extinct wavelength from the sample. UV-Vis-NIR spectroscopy is an absorption spectroscopy that works in the ultraviolet, visible and near infrared spectral region. This region of the electromagnetic spectrum produces the electronic transitions in the molecules that absorb it. When sample molecules are exposed to the incident light and if the energy of incident light matches with the energy required for a possible electronic transition in which an electron is promoted to the higher energy orbital, in that case some of the incident light will be absorbed by the sample molecules. These absorbed wavelengths are recorded by the spectrometer which provides a plot between these wavelengths and the degree of absorption.[7]

Experimental details:

GeO_2 thin films have been deposited on Si and quartz substrates using E- beam evaporation. Before the deposition, the Si and quartz substrates were cleaned thoroughly by using standard RCA cleaning process and thereafter dried using the heat blower to evaporate the moisture from the substrates. Subsequently, these substrates were put on the substrate holder in the vacuum chamber of electron beam evaporation machine 'Vacuum Coating Unit Model- BC- 300'. The pallets of GeO_2 having density 4.23 g/cm^3 were kept in a crucible and the chamber is evacuated using rotary and diffusion pumps to achieve a base pressure of the order of 10^{-5} mbar. The deposition was carried out by applying a fixed voltage and current of 4.84 kV and 6 mA, respectively. A thin film of 100 nm was deposited in 70 minutes at a deposition rate of 0.023 nm/sec.

The deposited thin films were annealed using Thermal CVD in Ar (95%) and H_2 (5%) environment at 650 ^{o}C for 30, 60 and 90 minutes. The identification of Raman modes was done using Raman spectroscopy at room temperature with a solid state laser operating at 532 nm. The study of transmittance was done using UV-Vis-NIR spectroscopy.

Results and Discussion

- **Raman Study:**

Raman spectra of as-deposited and annealed thin films which are annealed at different annealing times, are shown in **Figure 2**. The formation of Ge nanocrystals is confirmed from Raman spectroscopic results. The peak at 435 cm^{-1} is corresponding to GeO_2 while the peak at about 525 cm^{-1} corresponds to Si substrate. The films which were annealed at 650 ºC show a sharp and narrow intense peak at 299 cm^{-1}. This intense peak is attributed to the transverse optical phonon mode of Ge.[8,9,10,11] This is sufficient to indicate the good crystallinity of Ge nanocrystals. The variation in the size of the crystals along with the stress results in the shifting of Raman peak towards higher wave number that was affected by annealing.[12] The size of nanocrystals increases with increasing the annealing time. However, the intensity of the Raman peaks is observed to decrease for the samples annealed at longer duration which is probably due to linkage of Ge atoms with oxygen atoms forming the suboxides of Ge. Hence there is a decrease in concentration of Ge nanocrystals.

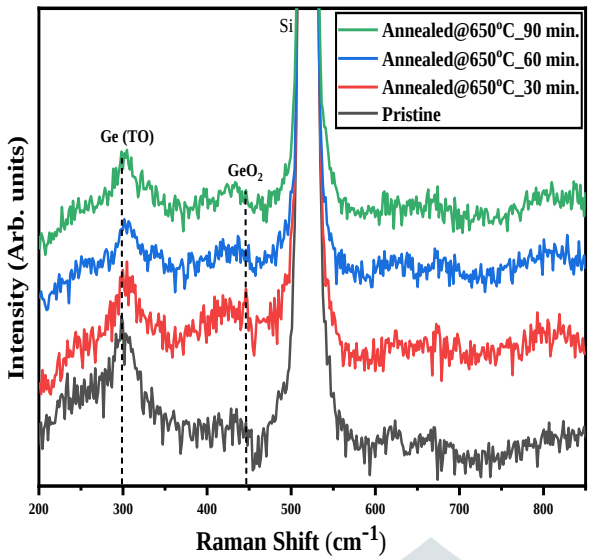

Figure 2: Raman spectra of as-deposited and annealed samples at 650 °C for 30, 60 and 90 minutes

- **UV-Vis-NIR Spectroscopy:**

UV-Vis spectra of as-deposited and annealed thin films which were annealed at different annealing times, are shown in **Figure 3**. The optical properties of the pristine and annealed samples were studied using this spectroscopy in the wavelength ranging from 200 to 2000 nm. It can be seen that there is decrease in the transmittance when the samples are annealed at 650 °C. The average transmittance of 80-90 % is observed for the as-deposited and annealed films, signifying that the quality of the deposited films is quite good. The change in transmittance can be due to the subsequent change in the content of oxygen in GeO_2 films. For the sample annealed for 30 minutes, it is observed that there is a sharp increase in transmittance at about 300 nm wavelength. In case of samples annealed for 60 and 90 minutes, this change is around 200 nm. The absorbance for the deposited samples is lying below this range of 200-300 nm.

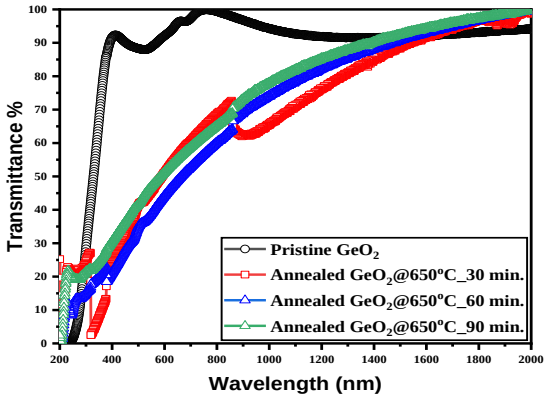

Figure 3: UV-Vis spectra of the pristine and annealed samples at 650 °C for 30, 60 and 90 minutes

Conclusion:

In summary, GeO_2 thin films were successfully synthesized using e-beam evaporation which is followed by annealing the prepared films at three different times of 30, 60 and 90 minutes keeping the annealing temperature fixed at 650 $^{\circ}$C. The effects of annealing time on structural and optical properties have been investigated using Raman spectroscopy as well as using UV-Vis-NIR spectroscopy. As a result of increasing the annealing time the transmittance was observed to decrease. Further the Ge nanocrystals were observed to arise in the GeO_2 matrix after annealing the films at 650 $^{\circ}$C while the concentration of Ge nanocrystals was observed to decease after increasing the annealing time from 30 to 90 minutes due to linkage of Ge atoms with oxygen atoms forming the suboxides of Ge. The transmittance decreases upon increasing the annealing temperature. The study shows a considerable effect of annealing time on the Ge nanocrystals growth in GeO_2 matrix and the optical properties of GeO_2 thin films.

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