Nanostructured multilayer TiO$_2$–Ge films with quantum confinement effects for photovoltaic applications

Abdul Faheem Khan$^a$, Mazhar Mehmood$^{a,*}$, Muhammad Aslam$^a$, Syed Ismat Shah$^b$

$^a$National Centre for Nanotechnology, Department of Chemical and Materials Engineering, Pakistan Institute of Engineering and Applied Sciences (PIEAS), Islamabad 45650, Pakistan
$^b$Department of Physics and Astronomy, University of Delaware, Newark, DE 19716, USA

**Abstract**

Multilayer TiO$_2$–Ge thin films have been deposited using electron beam evaporation and resistive heating. The thickness of the TiO$_2$ layers is 20 nm, while the thickness of the Ge layers varies from 2 to 20 nm with a step of 2 nm away from the substrate. These films were characterized by studying their optical, electrical, and structural properties. The films were annealed at various temperatures up to 500 °C for 2 h. The films are amorphous up to an annealing temperature of 400 °C, although Raman spectra suggest short-range ordering (and adjustments). The films annealed at 450 and 500 °C exhibit X-ray reflections of Ge and anatase TiO$_2$. Illumination in sunlight increases the conductivity of the as-deposited and annealed films. The band gap of the amorphous films changes from 1.27 to 1.41 eV up to 400 °C; the major contribution is possibly through direct transition. Two band gap regimes are clearly seen after 450 and 500 °C with abrupt increases at about 380 °C. The results imply that the TiO$_2$–Ge multilayer films may be employed as heterojunctions with tunable band gap energy as related to quantum confinement effects.

© 2009 Elsevier Inc. All rights reserved.

1. Introduction

The electronic and optical properties of nanomaterials and devices are strongly affected by quantum confinement effects related to size and shape of the nanostructures. Currently, a new generation solar cell concept has been born: the “third generation” based on nanostructured materials for their quantum confinement effects. The interest in the development of these materials is the potential to increase the efficiency of the photovoltaic devices by improving the coverage of the solar spectrum and reducing the energy losses of photon absorption [1–7].

Among such innovated materials, titania–germanium nanocomposites are currently under investigation by various workers [8,9]. Titania is a wide band gap semiconductor (3.2 eV), which means that it is mainly activated by ultraviolet (UV) light [10]. On the other hand, bulk germanium has a direct band gap of 0.8 eV and an indirect band gap of 0.66 eV [11] at room temperature. Formation of nanoparticles of germanium in the titania matrix shifts the absorption edge of germanium toward higher energies depending on the particle size [12], which may be exploited to maximize the conversion efficiency of titania–germanium photovoltaic devices.

In this work, multilayer titania–germanium thin films have been prepared and annealed at various temperatures. It has been shown that these films exhibit quantum confinement effects with tailorable band gap energy. Particular focus has been on the changes in structure, optical properties, and electrical properties with annealing temperature.

2. Materials and methods

Multilayer TiO$_2$–Ge thin films were fabricated using electron beam evaporation of TiO$_2$ powder (99.99%) and resistive heating of Ge powder (99.999%) as a starting material onto BK7 glass substrates. Ultrahigh purity oxygen (99.99%) was used as a reactive gas in order to backfill the chamber during deposition of TiO$_2$ layers. The partial pressure of O$_2$ was maintained below $2 \times 10^{-4}$ mbar. The flow of oxygen was controlled by a variable leak valve. The Ge layers were deposited by resistive heating using a tungsten crucible. The basic vacuum was pumped to less than $1 \times 10^{-5}$ mbar before deposition of Ge layers. Temperature of the substrate was maintained at 300 °C, it was rotated at 30 rpm, and source to substrate distance was kept as 35 cm.

First, a 20-nm layer of TiO$_2$ was deposited (in an oxygen environment) with an average deposition rate of 0.45 nm s$^{-1}$. A 2-nm
A layer of Ge was then deposited on TiO$_2$ with a rate of 0.15 nm s$^{-1}$. On the Ge layer, a second layer of TiO$_2$ of 20 nm was deposited and similarly 4-, 6-, 8-, 10-, 12-, 14-, 16-, 18-, 20-nm layers of Ge were deposited on each 20-nm layer of TiO$_2$. A final layer of TiO$_2$ (20 nm) was deposited on a 20-nm layer of Ge. Total thickness of films was 330 nm (TiO$_2$ = 220 nm, 11 layers; Ge = 110 nm, 10 layers). The thickness of each layer and rate of deposition were controlled by a quartz crystal monitor. The films composed of TiO$_2$ and Ge layers are termed "multilayer TiO$_2$–Ge" films. Thin films of pure TiO$_2$ and Ge with thickness of 460 nm and 110 nm, respectively, were also deposited on glass substrates, separately. These films are called "TiO$_2$ films" and "Ge films." The films were annealed at various temperatures ranging from 100 to 500 °C for a fixed time of 2 h. Optical transmittance and absorbance of the as-deposited and annealed multilayer films were recorded at room temperature by a Perkin Elmer UV/VIS/NIR Lambda 19 spectrophotometer in the wavelength range 300–2500 nm. Impedance spectroscopic (IS) measurements were made at room temperature using an Alpha-A high performance frequency analyzer (Novocontrol Technologies, Germany) in the frequency range 0.1 Hz–1 MHz. Silver paint electrodes were used at a separation of about 15 mm, while the width of the samples was about 10 mm. The contacts were allowed to dry for 24 h in air. Structure of these films was determined by X-ray diffraction and Raman spectroscopy.

![X-ray diffraction patterns](image1)

**Fig. 1.** X-ray diffraction patterns of (a) TiO$_2$–Ge multilayer films, as-deposited (1) and annealed for 2 h at 100 °C (2), 200 °C (3), 300 °C (4), 400 °C (5), 450 °C (6), 500 °C (7); (b) TiO$_2$ and Ge films, as-deposited and annealed at 400 °C.

![Raman spectra](image2)

**Fig. 2.** (a) Raman spectra of as-deposited and annealed multilayer TiO$_2$–Ge films. (b) Raman spectra of TiO$_2$ films, as-deposited and annealed at 400 °C films. (c) Raman spectra of Ge films, as-deposited and annealed at 400 °C.
recording X-ray diffraction (XRD) patterns at room temperature using a Bruker D8 Discover diffractometer equipped with Cu Kα radiation. The Raman spectra were obtained at room temperature using the confocal mode of micro-Raman spectrometer (MST-1000A, DongWoo Optron Co. Ltd., South Korea) under excitation with a HeCd laser beam at 442 nm. Surface morphology of the films was investigated by atomic force microscopy (AFM) using Quesant Universal SPM (Ambios Technology) employing contact mode using silicon nitride tips.

3. Results and discussion

3.1. XRD studies

The films deposited on BK7 glass substrates were physically stable. Cracks and blisters were not found even after annealing up to 500 °C. X-ray diffraction studies can provide information on structural details, e.g., phases formed in the film. Fig. 1a shows XRD patterns of the as-deposited and annealed TiO₂–Ge multilayer films. All the films are amorphous except the films annealed at 450 and 500 °C. Annealing at 450 °C and above results in crystallization of these films to form anatase TiO₂ and cubic Ge (Fig. 1a). The anatase TiO₂ has a tetragonal I structure (I41/amd (141)) [13], exhibiting lattice parameters of \( a = b = 3.7836 \, \text{Å}, \ c = 9.4743 \, \text{Å} \) with unit cell volume of 135.63 Å³. While Ge has a cubic F structure (F(225)) [13] with lattice parameters: \( a = b = c = 5.6386 \, \text{Å} \) with unit cell volume of 179.27 Å³.

For comparison with the multilayer TiO₂–Ge films, thin films of pure TiO₂ (99.99%) and Ge (99.999%) with thickness of about 460 and 100 nm, respectively, were also deposited, separately, on glass substrates. XRD patterns of these films are shown in Fig. 1b, respectively. Note that the as-deposited TiO₂ film is crystalline. The as-deposited Ge film is amorphous, although it crystallizes to form cubic Ge after annealing at 400 °C. Fig. 1b suggests the general tendency of TiO₂ to deposit in the crystalline state and Ge in the amorphous state under the deposition conditions employed in this work.

TiO₂ layers with a thickness of 20 nm in the as-deposited TiO₂–Ge multilayer films (Fig. 1a) do not exhibit any crystalline phase contrary to the 460-nm thick TiO₂ film (Fig. 1b). This may be related to the fact that the structure of thin films (or layers in the multilayer films) may depend on thickness [14]. Furthermore, the amorphous structure of underlying Ge layers may also be responsible for the formation of the amorphous phase in thin TiO₂ layers, being deposited alternatively.

3.2. Raman studies

Raman studies provide information on the nature of bonds, which are affected by the structure of a particular phase and local atmosphere around atoms. Fig. 2a shows Raman spectra of the TiO₂–Ge multilayer films before and after annealing. A series of peaks are visible in the spectrum of the as-deposited film at about 306, 414, and 612 cm⁻¹. The peak at 306 cm⁻¹ can be assigned to
Ge [15], while the other two peaks belong to TiO$_2$ [16]. The TiO$_2$ peak at $\sim$414 cm$^{-1}$ shifts toward smaller wavenumbers of about 408, 400, 397, and 394 cm$^{-1}$ and the peak at $\sim$612 cm$^{-1}$ shifts toward higher wavenumbers of about 615, 625, 629, and 630 cm$^{-1}$ for the films annealed at 200, 400, 450, and 500 °C, respectively. This is also accompanied by gradual emergence of a new peak at
510 cm\(^{-1}\) after annealing at 200 °C and above. This peak can also be assigned to TiO\(_2\) [16]. These changes occurring at annealing temperatures of 200–400 °C suggest short-range ordering in the amorphous TiO\(_2\) phase.

Raman spectrum obtained from 460-nm thick TiO\(_2\) films is shown in Fig. 2b, which exhibits peaks at 400, 510, and 625 cm\(^{-1}\) before and after annealing at 400 °C. The peak positions have a close match with anatase TiO\(_2\) [16]. It may further be noted that the peak positions exhibited by 460-nm thick TiO\(_2\) film (Fig. 2b) are different from those corresponding to TiO\(_2\) in the TiO\(_2\)–Ge multilayer films (Fig. 2a), even after complete crystallization to form anatase TiO\(_2\). Furthermore, the Raman peaks of TiO\(_2\) in the TiO\(_2\)–Ge multilayer films are also significantly broader in comparison with the TiO\(_2\) film, which may be due to quantum confinement effects, nanocrystallinity, and large interfacial areas [17].

Raman spectra of 110-nm thick Ge films are also shown in Fig. 2c, before and after annealing at 400 °C. Peak position lies at about 297 cm\(^{-1}\), which is lower than that exhibited by Ge in the multilayer films, i.e., 305 cm\(^{-1}\), as shown in Fig. 2a. It appears that large interface (surface) areas in the multilayer films have resulted in strained (and dangling) bonds such that Raman peak positions appear at higher wavenumbers in comparison with the Ge film [15].

### 3.3. AFM studies

AFM can be used to study the surface morphology at an extremely high resolution. For an optical surface (coating), roughness is normally considered as an important parameter. Surface roughness not only describes the light scattering but also gives an idea about the quality of the surface under investigation, in addition to providing some insight on the growth morphology. Three-dimensional AFM images of the glass substrate, as-deposited and annealed TiO\(_2\)–Ge multilayer films are shown in Fig. 3. Surface features of the films are different from those appearing on the substrate. Protuberances of the order of 10 nm in height and about 20 nm in width can be seen in the as-deposited films. These features are of the order of individual layer thickness. The morphology does not change significantly up to an annealing temperature of 400 °C. Smoothening of the surface occurs at 450 °C, possibly due to ordering of atoms in order to reduce surface energy. Rough morphology after annealing at 500 °C may be due to the formation of wrinkles associated with (substantial) crystallization and associated transformation stresses.

### 3.4. Optical studies

Fig. 4 shows transmittance of the as-deposited and annealed TiO\(_2\)–Ge multilayer films as a function of wavelength. For comparison, transmittance of the as-deposited TiO\(_2\) and Ge films has also been included. The absorption edge of the as-deposited multilayer film is close to that of Ge film, which slightly shifts toward smaller wavelengths after annealing up to 300 °C, as shown in Fig. 4a. However, a pronounced blue shift in the absorption edge is observed after annealing at 350 °C and above (Fig. 4b).

Fig. 5 shows absorption coefficient (\(\alpha\)) of the as-deposited and annealed multilayer films, as a function of photon energy (\(h\nu\)). A straight line can be easily fitted, extending over a wide range of wavelengths for the films annealed up to 400 °C. The band gap energy changes from 1.27 eV for the as-deposited TiO\(_2\)–Ge multilayer film to about 1.41 eV for the film annealed at 400 °C. Two straight line regions are clearly seen in the plots of the films annealed at 450 and 500 °C. These may arise from an indirect band gap at about 1.2 eV, and a direct band gap at 1.72 and 1.77 eV for the films annealed at 450 and 500 °C, respectively. A close examination of the plots for the films annealed up to 400 °C also points out an additional band gap at about 1.1–1.2 eV, although it is negligible as far as its absorption activity is concerned. It appears that the Ge layers in the multilayer films manifest themselves predominantly as direct band gap materials, the absorption activity at the indirect band gap (1.1–1.2 eV) being insignificant, particularly up to an annealing temperature of 400 °C, in contrast to bulk Ge that is predominantly an indirect band gap material. This is an interesting aspect arising from quantum confinement effects in nanostructured Ge layers.

It is well-known that band gap energy of thin films changes with film thickness [14], deposition techniques [18], and annealing [19], which is because of the formation of nanoparticles [14], nanoporosity [20], and an oxide network [15,19] causing quantum confinement effects associated with nanostructures [14,15,19]. It has been shown earlier that nanostructured Ge films exhibit quan-
Quantum confinement effects [14,15,19], and annealing of Ge films causes blue shift in photo-absorption (from 1.1 eV to about 1.35 eV) due to enhanced quantum confinement effects. On the other hand, a band gap of Ge in the present TiO₂–Ge multilayer films exhibits a more pronounced shift with annealing with a very significant increase to about 1.72 and 1.77 eV after crystallization at 450 and 500 °C, respectively. This pronounced effect may be due to TiO₂ in the multilayer films that tend to isolate Ge crystallites/islands and layers from each other for enhanced quantum confinement effects. It is well-known that three-dimensional quantum confinement in nanoparticles is much more effective than one-dimensional quantum confinement in 2-D layers [14]. The pronounced increase with annealing in our multilayer films seems to arise from gradual conversion of 2-D layers into 3-D islands, crystallites, or quantum dots partly isolated from each other by TiO₂.

3.5. Electrical and optoelectronic studies

Impedance spectroscopy (IS) can be used to characterize intrinsic electrical properties of a material or films. The basis of IS is the analysis of the impedance of the system under investigation based on applied frequency, voltage, current, and phase shift between voltage and current signals. Data obtained by IS measurements are often expressed in terms of a Nyquist plot, i.e., Z’ (imaginary part of impedance) vs. Z’’ (real part of impedance). Bode plots describe various parameters in terms of frequency.

The complex impedance spectra (Z’ plotted against Z’’) (Nyquist plots) for the as-deposited and annealed multilayered TiO₂–Ge films were recorded while illuminating in the sunlight as well as in the dark, as shown in Figs. 6 and 7, respectively. The complex impedance plot of the as-deposited Ge thin film has also been included, for reference. Each IS plot shows only one depressed semi-circle. The semicircles are depressed due to the distribution of relaxation time and therefore show the non-Debye nature of the films [21,22]. The tail trend observed at lower frequencies is due to the electrode effects [23]. It may be noted that the electrical behavior of the multilayer films is strongly dependent on annealing temperature.

These results have been analyzed, as presented in Fig. 8, which shows typical Nyquist (Fig. 8b) and Bode plots (Fig. 8c and d), comparing the measured data with simulated curves. The simulated curves are based on a circuit that comprises a constant phase element (CPE) in series with a parallel combination of resistance.

![Fig. 5. Plots of absorption coefficient, α, vs. photon energy (hv) of TiO₂–Ge multilayer films.](image-url)
and capacitance (Fig. 8a). A close match between the measured and the simulated curves is clearly seen. The intercept on the real impedance axis ($Z_0$) in the fitted Nyquist plots gives dc resistance from which conductivity of the films has been calculated. The conductivity ($\sigma$) of the multilayer films is shown in Fig. 9, as a function of annealing temperature ($T_A$).

As shown in Fig. 9, the conductivity increases as the films are exposed to sunlight (irrespective of annealing temperature) in comparison with measurements in the dark, indicating an increase in the charge carrier density due to absorption of photons. Although not shown here, the conductivity of the as-deposited and annealed multilayer films is higher than that of the as-deposited Ge films. This seems to be due to synergistic effects at the interface. Conductivity increases with annealing temperature, which may partly be due to removal of structural defects, and (short- and long-range) atomic ordering. Improvement in the short-range ordering of the films with annealing has also been evident from the Raman spectra (Fig. 2a) developing peaks.
of anatase TiO$_2$ well below the crystallization temperature. A substantial rise in conductivity is observed at about 380 °C. The films remain amorphous up to annealing temperature of 400 °C, as can be seen in Fig. 1a. Therefore, it may be inferred that a rise in conductivity may be associated with changes in the properties of heterojunction composite film. It has also been found that the band gap changes with annealing temperature (Fig. 5), with noticeable changes in absorption spectra above...
300 °C (Fig. 4b). Such changes may adjust the relative positions of the band edges so that a pronounced drop of electrons may be possible into the conduction band of TiO$_2$, hence increasing the concentration of the charge carriers (and their lifetime) and causing an increase in conductivity.

As a preliminary investigation, photovoltaic I–V response of the as-deposited multilayer film was also obtained, as shown in Fig. 10; the device configuration being shown in the inset. The multilayer TiO$_2$–Ge films demonstrate a photovoltaic response. Further investigation to optimize the synthesis, heat treatment, thickness of the films, substrate temperature, and electrode materials is underway.

4. Discussion

Vapor-deposited Ge films exhibit higher band gap energy [14,15,19], in comparison with bulk Ge (~0.7 eV). Gorokhov et al. [15] have found that higher band gap energy is due to small particle size of Ge crystals isolated by a minute amount of oxide. Tripathi et al. [14] have related the changes in band gap with the size of nanoparticles and clusters that varies with thickness of Ge films. Calderon et al. [20] have shown that quantum confinement effects are also caused by nanoporosity in the Ge films. The band gap of Ge films has also been shown to change with annealing and oxide formation [19].

The band gap of as-deposited TiO$_2$–Ge multilayer film is about 1.27 eV, which is higher than that of Ge film (1.1 eV) [19]; the large-band-gap TiO$_2$ layers isolating the Ge layers seem to enhance the quantum confinement. The band gap further increases with annealing up to about 1.41 eV at an annealing temperature of 400 °C and it comes out to about 1.8 eV after crystallization at 450 and 500 °C. The increase in band gap suggests an increase in quantum confinement owing to diffusion and adjustments that lead to gradual conversion of 2-D layers into 3-D clusters by roughening, although significant change has been possible only after complete crystallization at 450 and 500 °C.

The multilayer films exhibit higher conductivity when exposed to sunlight in comparison with the dark. This is because of an increase in the concentration of charge carriers by illumination. It is worth noting that the conductivity of the as-deposited multilayer film is higher than that of the as-deposited Ge film (Fig. 6), despite the fact that the total thickness of the semiconductors was the same in both cases (i.e., 110 nm). This suggests the formation of a heterojunction composed of Ge and TiO$_2$ layers in the multilayer films. Due to band bending at the interface, holes seem to drop into the valence band of Ge and the electrons into the conduction band of TiO$_2$. This results in an increase in the charge carrier density and thus conductivity of the multilayer films in comparison with Ge film. A pronounced increase in conductivity of the multilayer films is observed at annealing temperatures of 380 °C and above (Fig. 9). This seems to be related to changes in the properties of heterojunction. For instance, the band gap increases (Fig. 5) and the absorption edge shifts toward smaller wavelengths with annealing temperature particularly above 300 °C (Fig. 4b). The changes in band gap and associated adjustments in the relative levels of the band edges of Ge with respect to TiO$_2$ in the film seem to improve the heterojunction characteristics of multilayer TiO$_2$–Ge film for more efficient transfer of electrons to TiO$_2$ and the holes to Ge required for increased charge carrier density.

Variations in the thickness of Ge layers along the depth of the film seem to be responsible for slow change in absorption near the band edge, as related to size-dependent quantum confinement effects. This may be useful for more efficient solar absorption.

5. Summary

- TiO$_2$–Ge multilayer films have been deposited using electron beam evaporation and resistive heating. The thickness of each TiO$_2$ layer was 20 nm, while the thickness of the Ge layers varied from 2 to 20 nm away from the substrate with a step of 2 nm.
- The as-deposited multilayer films were amorphous in nature. Annealing at 450 and 500 °C resulted in crystallization to form anatase TiO$_2$ and cubic Ge as revealed by XRD studies, although Raman studies suggested short-range ordering in the amorphous structure at much lower annealing temperatures.
- Annealing caused changes in absorption spectra. The direct band gap energy of 1.27 eV for the as-deposited film gradually increased with annealing temperature, up to 1.41 eV for the (amorphous) film annealed at 400 °C. A drastic increase up to 1.77 eV was observed by crystallization at 500 °C.
- The films exhibited higher conductivity if illuminated in sunlight in comparison with measurements in the dark. The conductivity of the as-deposited (multilayer) film was higher than that of the Ge film. The conductivity increased further with annealing showing a substantial rise at annealing temperature of 380 °C and above.
- The results suggest that the as-deposited and annealed multilayer TiO$_2$–Ge films function as heterojunction materials with quantum confinement effects. Annealing can help in band gap engineering to improve the characteristics of this heterojunction material.

Acknowledgment

The authors are thankful to the Higher Education Commission (HEC), Government of Pakistan for the financial support.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcis.2009.11.045.

References

[14] The Joint Committee on Powder Diffraction Standards (JCPDS), Cards No. 00-021-1272 and 03-065-9209, by International Centre for Diffraction Data (ICDD), Swarthmore, PA, USA.