

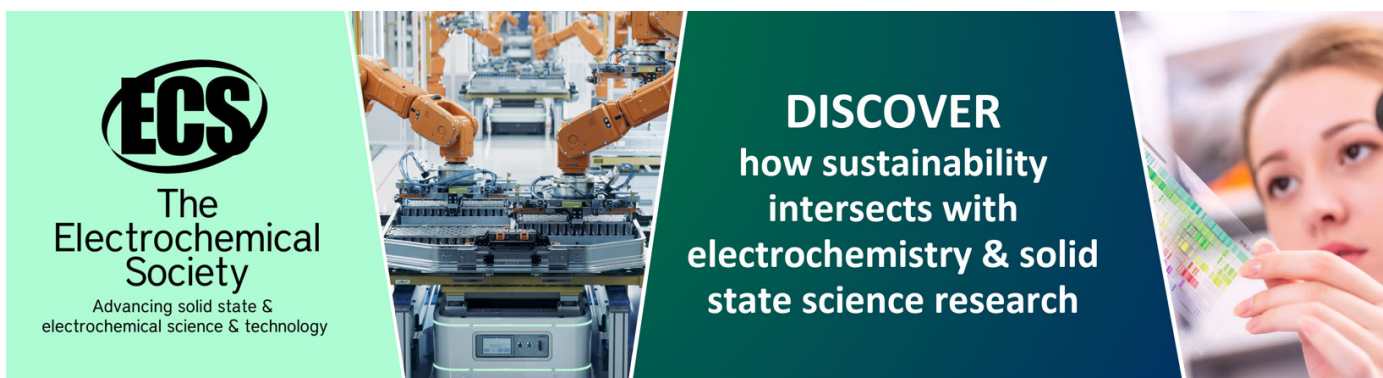
## Titania–germanium nanocomposite for photo-thermo-electric application

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# Titania–germanium nanocomposite for photo-thermo-electric application

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## Abstract

The introduction of germanium (Ge) into titania ( $\text{TiO}_2$ ) creates an attractive semiconductor. The new semiconductor is named titania–germanium ( $\text{TiO}_2\text{--Ge}$ ). Ge dots are dispersed in the distorted  $\text{TiO}_2$  matrix of  $\text{TiO}_2\text{--Ge}$ . The quantum Bohr radius of Ge is 24.3 nm, and hence the properties of the Ge dot can be varied by tailoring its size if it is smaller than its Bohr radius due to the quantum confinement effect (QCE). Therefore, simply by changing the Ge concentration, the morphology of  $\text{TiO}_2\text{--Ge}$  can be varied within a wide range. Consequently, the optical, electronic and thermal properties of  $\text{TiO}_2\text{--Ge}$  can be tailored.  $\text{TiO}_2\text{--Ge}$  becomes a promising material for the next generation of photovoltaics as well as thermoelectric devices. It could also be used for photo-thermo-electric applications.

## 1. Introduction

In recent years, the energy crisis has become one of the main global concerns. Fossil fuel prices are continuously increasing. In addition, environmental problems caused by the use of conventional fuels have already reached warning levels. Therefore, we need to use renewable energy sources to solve our global energy problem [1]. Among different non-conventional energies, solar and thermal energies, which are abundant in the earth, could be good alternatives to conventional energies. To solve the energy challenge by utilizing these renewable energy sources we have to find appropriate cost-effective and environmentally stable technologies. For this purpose, several research groups are endeavoring to find new materials as well as technologies [2–4].

In obtaining a breakthrough in solar energy conversion, the development of quantum dot (QD) materials and the technologies of their solar cells already set a promising start. Quantum dots have the unique ability of multiple exciton (electron–hole pair) generation per photon of energy absorbed [5], while conventional semiconductors can generate just one electron–hole pair per photon. In other words, QD materials can eliminate many of the energy losses of photon absorption associated with traditional semiconductors.

As with optoelectronic applications, semiconductor quantum dots are attractive for thermoelectric application, too. This is because their confined low-dimensional structures block the phonons, and transmit the electrons that could help to enhance the thermoelectric figure-of-merit. Recent research developments show that Si/Ge superlattice [6–8] and Ge dots in  $\text{SiO}_2$  [9, 10] are the most promising next generation thermoelectric materials. The thermal conductivities of those nanostructured materials are about an order of magnitude lower than those of bulk semiconductors, and hence the thermoelectric figures-of-merit of nanostructured systems enhance. Moreover, the syntheses of QD materials are relatively inexpensive and simple compared to the manufacturing of conventional photovoltaic and thermoelectric materials.

In the present innovative approach, the author would like to enter into a novel field of research: photo-thermo-electric application of QD materials. The specialty of this field of research is that QD materials could simultaneously convert solar and thermal energies into electrical energy. As a consequence, the efficiency of electricity generation would be enhanced. In this perspective, a new QD semiconductor, titania–germanium ( $\text{TiO}_2\text{--Ge}$ ), has been introduced [11–14]. The structural, optical, electrical and thermal properties of thermodynamically stable  $\text{TiO}_2\text{--Ge}$  thin films have been studied. The study shows that the different properties (structural, optical, electrical and thermal) of  $\text{TiO}_2\text{--Ge}$  could be customized in a wide range by varying the Ge

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concentration in it, and that  $\text{TiO}_2\text{-Ge}$  could be a next generation optoelectronic and thermoelectric semiconductor. In other words,  $\text{TiO}_2\text{-Ge}$  would be an ideal QD semiconductor for photo-thermo-electric applications.

## 2. Experimental details

### 2.1. Processing of $\text{TiO}_2\text{-Ge}$ films

$\text{TiO}_2\text{-Ge}$  thin films were synthesized by RF magnetron sputtering. For the preparation of sputtered films, several  $\text{TiO}_2\text{-Ge}$  composite targets, namely C1, C2, C3, C4, C5, C6, C7 and C8, were used. The composite targets were fabricated from a mixture of  $\text{TiO}_2$  (P25 Degussa, 70% anatase, 99.8% purity, average particle size 30 nm, and specific surface of  $50 \text{ m}^2 \text{ g}^{-1}$ ) and Ge ( $\sim 100$  mesh, 99.99% pure). The wt% of Ge in C1, C2, C3, C4, C5, C6, C7 and C8 was 1, 2, 3, 4, 5, 9, 15 and 33, respectively. Sputtering was carried out in an inert atmosphere of 6 mTorr argon (Ar) while the base pressure of deposition chamber was  $5 \times 10^{-7}$  Torr. Films were deposited at room temperature on different substrates, such as quartz, lacy carbon grids, and silicon wafers, for different characterizations using RF power ( $P_w$ ) of 150 W followed by annealing at temperatures ( $T_a$ ) of  $700^\circ\text{C}$ .

### 2.2. Characterizations

For the structural characterizations of  $\text{TiO}_2\text{-Ge}$  films, x-ray diffraction (XRD), x-ray photo-thermal spectroscopy (XPS), and transmission electron microscopy (TEM) were used. The XRD data of the nanocomposite films were collected by using a Rigaku D-Max B horizontal diffractometer. SSI-M probe XPS was used employing  $\text{Al K}\alpha$  ( $h\nu = 1486.6 \text{ eV}$ ) exciting radiation to study the chemical state of Ge and Ti as well as to obtain the cation composition of films. JEM 2010F TEM was utilized to examine the microstructure of films as well as to obtain the particle size, film composition and crystal structure. For analyzing the composition and structure, high-angle annular dark field (HAADF) and bright field imaging techniques were exploited. The HAADF technique involves collecting electrons that have been forward scattered through high angles, typically a few degrees or more, to form images. The scattering, and hence the image, depend largely on the difference between the atomic numbers of elements. The brighter spots represent the heavier atomic number element while the less intense spots indicate the lighter atomic number element.

Optical transmission and reflection data in the wavelength range of 200–2600 nm were obtained with a UV-VIS-NIR PerkinElmer spectrophotometer, and the optical gaps of nanocomposite films were determined by the Tauc method using these data. The dark conductivities and photoconductivities were measured in an environmental test chamber. The photoconductivity was measured under  $50 \text{ mW cm}^{-2}$  white light from a tungsten halogen lamp.

p-Si/ $\text{TiO}_2\text{-Ge}$  heterojunction solar cells were fabricated with a device structure of Al/p-Si/ $\text{TiO}_2\text{-Ge}$ /ITO. To fabricate the heterojunction solar cells,  $\text{TiO}_2\text{-Ge}$  layers were deposited on p-type (111) oriented floating-zone crystalline silicon (c-Si)

( $2 \Omega \text{ cm}$ ,  $400 \mu\text{m}$ ) substrates. Aluminum (Al) was evaporated on the p-Si/ $\text{TiO}_2\text{-Ge}$  heterojunction to make the back contact of the solar cell, followed by an annealing at  $550^\circ\text{C}$  under nitrogen environment, ensuring a good ohmic contact between wafer and Al. The ITO dots ( $0.080 \text{ cm}^2$ ) were used as the front contacts. Current–voltage ( $I\text{-}V$ ) characteristics of those heterojunction solar cells were measured under the AM 1.5 solar radiation of  $100 \text{ mW cm}^{-2}$  by an Oriel solar simulator. The external quantum efficiency (IPCE) spectra of the solar cells were measured under the short circuit condition using a lock-in amplifier and chopped monochromatic light.

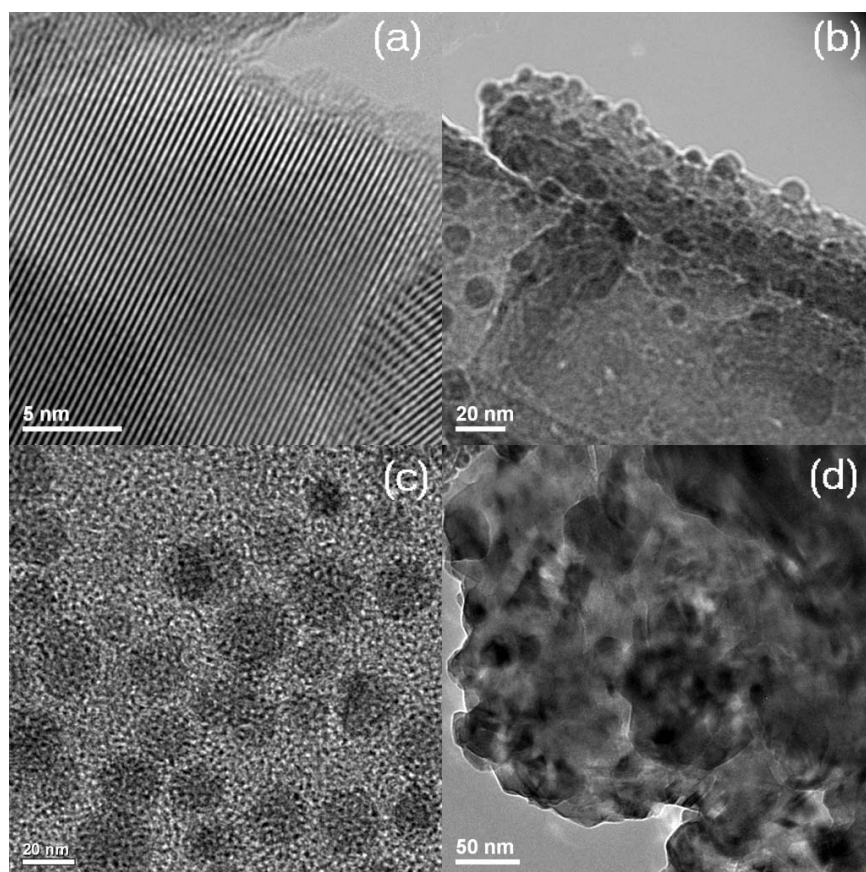
Thermal conductivity has been estimated by using axial heat flow method. Two references (Ge and  $\text{TiO}_2$  films) have been used; the thermal conductivities of the films were determined in a comparison study with each reference.

## 3. Results and discussion

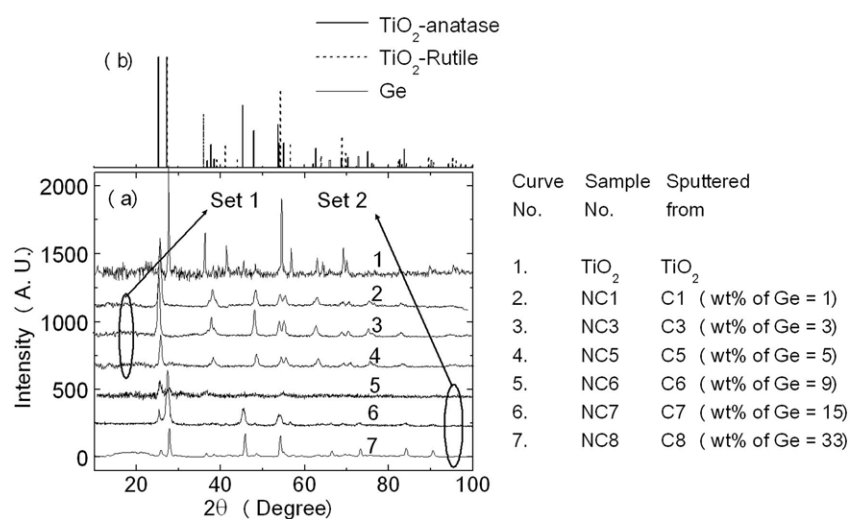
### 3.1. Morphology

The nanocomposite films sputtered from C1, C2, C3, C4, C5, C6, C7 and C8 were named as NC1, NC2, NC3, NC4, NC5, NC6, NC7 and NC8, respectively. All of these samples were characterized by transmission electron microscopy (TEM) for their structural analysis. Figures 1(a)–(d) present transmission electron micrographs of NC5, NC6, NC7 and NC8, respectively. The high-resolution bright field (BF) image in figure 1(a) reveals that NC5 is a single-phase nanocrystalline sample. The transmission electron micrographs of NC1, NC2, NC3 and NC4 looked the same as that of NC5, and so these are not included in the figure. On the other hand, the transmission electron micrographs of NC6, NC7 and NC8 consist of black spots in a gray matrix, as shown in figures 1(b)–(d). Those black spots were identified as Ge dots by HAADF imaging and energy dispersive x-ray spectroscopy (EDXS), and the sizes of the black spots for NC6, NC7 and NC8 are 7, 15 and  $>17$  nm, respectively. Due to the distinct morphological difference observed in figure 1, the NC samples are divided into two sets: set 1 includes NC1, NC2, NC3, NC4 and NC5, while set 2 comprises NC6, NC7 and NC8.

To obtain the comprehensive morphological information (stoichiometries and compositions) of the nanocrystalline phases of set 1 samples or the gray matrices and the black spots of set 2 samples, x-ray diffraction (XRD) patterns of the NC samples were studied; see figure 2. Figure 2(a) shows the XRD patterns of  $\text{TiO}_2$  and  $\text{TiO}_2\text{-Ge}$  samples calcined at  $700^\circ\text{C}$ . Figure 2(b) includes the standard XRD peak positions of  $\text{TiO}_2$  anatase,  $\text{TiO}_2$  rutile and Ge, which help us to identify the stoichiometries of nanoparticles. It is found in figure 2(a) that NC1, NC3 and NC5 have a polycrystalline  $\text{TiO}_2$  anatase structure with (101), (103), (004), (112), (200), (105) and (211) diffraction peaks. The anatase structures of Ge-added  $\text{TiO}_2$  samples were also confirmed by a selected area electron diffraction patterns analysis. However, the simple  $\text{TiO}_2$  films, calcined at the same temperature ( $700^\circ\text{C}$ ), have nanoparticles with a mixed polycrystalline phase of rutile and anatase. The erratic behaviors of XRD patterns of NC1, NC3 and NC5 will



**Figure 1.** Transmission electron micrographs of  $\text{TiO}_2$ -Ge films: BF images of (a) NC5: sputtered from C5 (Ge = 5 wt%), (b) NC6: sputtered from C6 (Ge = 9 wt%), (c) NC7: sputtered from C7 (Ge = 15 wt%) and (d) NC8: sputtered from C8 (Ge = 33 wt%).



**Figure 2.** X-ray diffraction study of  $\text{TiO}_2$ -Ge films: (a) XRD patterns in the  $2\theta$  range of  $10^\circ$ – $100^\circ$ , (b) the standard XRD peak positions of  $\text{TiO}_2$  anatase,  $\text{TiO}_2$  rutile and Ge.

be discussed later. Set 2 samples show the Ge (111), (220), (311), (400) diffraction peaks, along with the  $\text{TiO}_2$  anatase reflections. The x-ray diffraction intensities of the Ge peaks become stronger, and the full width at half maximum (FWHM) values of those peaks become sharper, with the increase of Ge wt% in the sputtering target for the set 2 samples. These facts indicate the size enhancement of Ge nanodots. The crystallite

sizes of Ge and  $\text{TiO}_2$  were calculated by using Scherrer's formula [15]. The determined sizes of Ge nanodots in NC6, NC7 and NC8 are 7, 15 and 17 nm, respectively. The average sizes of  $\text{TiO}_2$  particles in different samples range from 18 to 20 nm. The size increments of Ge nanodots for the set 2 samples have already been visualized in the transmission electron micrographs (figure 1). In fact, this is obvious,



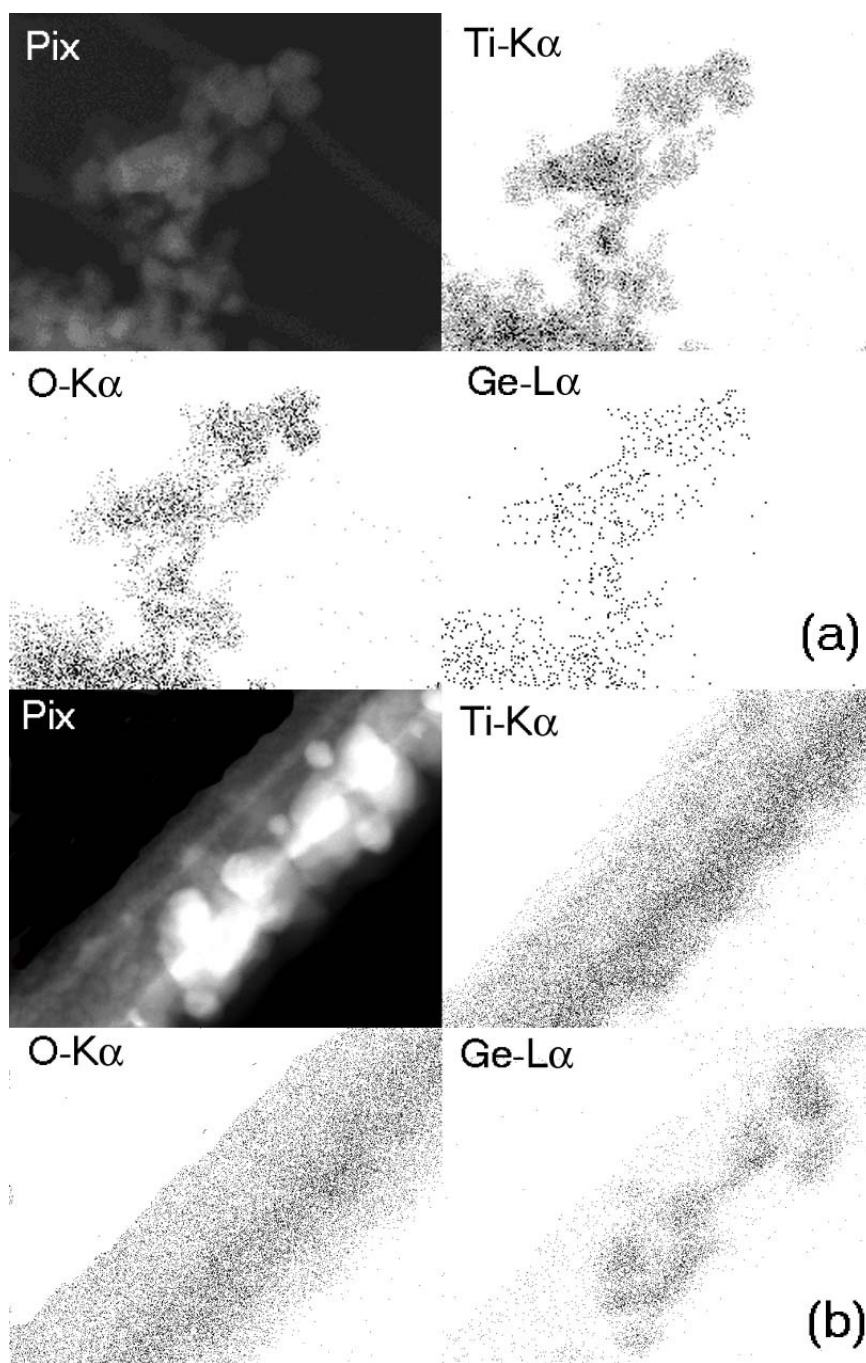
because the composition and morphology of a sputtered film is governed by the composition of the sputtering target [16]. NC7 and NC6 were sputtered from the composite targets C7 and C6, respectively, and the Ge concentration of C7 is higher than that of C6. Therefore, NC7 has bigger Ge dots than NC6. The further increase of Ge concentration in the composite target causes the abundance of Ge in NC8, and the overlapping of crystalline planes for Ge polycrystals [12] has been viewed in the micrograph of figure 1(d).

At this point, the combination of TEM and XRD studies convince us that one phase of set 2 nanocomposite samples is Ge nanodots, and the XRD patterns show that the other phase of set 2 samples or the nanocrystalline phase of set 1 samples is  $\text{TiO}_2$  anatase. Since the processing temperature of set 1 and set 2 samples is  $700^\circ\text{C}$ , the presence of a mixture of  $\text{TiO}_2$  rutile and anatase is expected in both sets of samples. Normally, undoped  $\text{TiO}_2$  films have the pure anatase structure at  $600^\circ\text{C}$ . The rutile phase begins to appear between  $650$  and  $750^\circ\text{C}$ . Between  $800$  and  $850^\circ\text{C}$ , the sample completely converts into the rutile structure [17–19]. In the present work too, undoped  $\text{TiO}_2$  films calcined at  $700^\circ\text{C}$  have a mixed phase of rutile and anatase structures. But, Ge-added  $\text{TiO}_2$  films processed at  $700^\circ\text{C}$  have strange properties. Only the  $\text{TiO}_2$  anatase structure was identified in all the NC samples. Such inconsistent behaviors have also been noticed for other doped  $\text{TiO}_2$  nanoparticles [20–22]. The local structures of dopants may distort the  $\text{TiO}_2$  lattice, which results in the unusual properties of the nanoparticles. For that reason, we need to elucidate the compositions of the matrix of set 2 films and the nanocrystalline phase of set 1 samples. To visualize the elemental compositions in both sets of films, HAADF imaging, EDXS, and energy dispersive spectroscopic x-ray mappings were done. Figures 3(a) and (b) present the HAADF image and the elemental mappings of Ti, O and Ge for a set 1 sample (NC5) and a set 2 sample (NC8), respectively. The nanocrystalline phase of NC5 has a uniform distribution of elements Ti, O and Ge, while NC8 has Ge nanodots in the matrix made up of uniformly distributed Ti, O and Ge. Hence, the elemental mappings show us that the nanocrystalline phase of set 1 samples or the matrix of set 2 samples is a Ge-added  $\text{TiO}_2$  lattice.

If Ge is incorporated into  $\text{TiO}_2$ , it should distort the  $\text{TiO}_2$  lattice; the lattice distortion of  $\text{TiO}_2$  can easily be identified by a detailed study of the XRD peaks from the nanocrystals. For this purpose, the (101) and (200) anatase peaks of  $\text{TiO}_2$  and  $\text{TiO}_2$ -Ge samples were comprehensively studied. These two peaks of  $\text{TiO}_2$ , NC1, NC3, NC5, NC6 and NC8 are displayed in figures 4(a) and (b), respectively. It is seen in figure 4 that both the peak positions slightly shift to higher angles with the increase of Ge concentration. The peaks' shifts have been observed for the films NC1–NC6. Surprisingly, the  $\text{TiO}_2$  anatase peaks of set 2 samples remain in the same peak positions. The lattice constants of Ge-added  $\text{TiO}_2$  for all NC samples were calculated based on the anatase (101) and (200) diffraction peak positions and the characteristics of anatase tetragonal structure. The lattice constant decreases with the increase of Ge concentration along the  $c$ -axis, only. The lattice constant  $a$  along the basal plane remains more or less constant.

The maximum shortening of  $c$ -axis is about  $0.48 \text{ \AA}$ . The lattice contraction determined from XRD is a sign of the possibility of  $\text{Ge}^{4+}$  ions substituting  $\text{Ti}^{4+}$  sites. Since the ionic radii of  $\text{Ge}^{4+}$  ( $r^{\text{IV}} = 0.039 \text{ nm}$ ,  $r^{\text{VI}} = 0.053 \text{ nm}$ ) [23, 24] is smaller than that of  $\text{Ti}^{4+}$  ( $r^{\text{IV}} = 0.042 \text{ nm}$ ,  $r^{\text{VI}} = 0.0605 \text{ nm}$ ) [23, 24], a lattice contraction takes place, and it enhances from NC1 to NC6. However, the anatase peaks for NC6 and NC8 are surprisingly situated at the same position, as seen in figures 4(a) and (b), though the Ge concentration of NC8 is much higher than that of NC6. This means that the lattice constants of Ge-added  $\text{TiO}_2$  for NC6, NC7 and NC8 are the same. Actually, the amount of addition of Ge atoms into the  $\text{TiO}_2$  lattice is restricted by the maximum equilibrium solid solubility limit of Ge atoms into the  $\text{TiO}_2$  nanoparticles. Therefore, when the concentration of Ge in  $\text{TiO}_2$ -Ge films crosses that limit, Ge atoms start to agglomerate as Ge nanodots that facilitate developing the nanocomposite films. As a consequence, NC6, NC7 and NC8 consist of Ge nanodots in the matrix of Ge-added  $\text{TiO}_2$  whereas the samples NC1 to NC5 have single-phase materials made up of Ge-added  $\text{TiO}_2$  nanoparticles.

To confirm the morphological information on the  $\text{TiO}_2$ -Ge films obtained by TEM and XRD studies, Raman experiments were carried out for various  $\text{TiO}_2$ -Ge films. Figure 5 displays the Raman shift spectra of  $\text{TiO}_2$  and  $\text{TiO}_2$ -Ge films calcined at  $700^\circ\text{C}$  (figure 5(a)). It also includes the ideal Raman scatterings of Ge and  $\text{TiO}_2$  (figure 5(b)). The Raman scattering features of  $\text{TiO}_2$  film is typical; it includes various optic modes of anatase (A) and rutile (R) structures [25, 26]. However, the Raman spectra of NC1, NC3, NC5, which comprise Ge-added  $\text{TiO}_2$  nanoparticles, seem different. These spectra only include the optic modes of the anatase structure. This implies that the Ge-added  $\text{TiO}_2$  samples have only the anatase phase, which was already predicted by the XRD study. Moreover, the anatase Raman bands become broadened and shifted towards the lower wavenumber side with increasing Ge concentration in the film. This particular fact reveals that the inclusion of Ge makes a stoichiometric change in the  $\text{TiO}_2$  lattice. The progressive structural change has been experienced for the samples NC1–NC6, as seen in figure 5. The Raman bands of Ge-added  $\text{TiO}_2$  for NC6 and NC7 remain in the same positions. This implies that the lattice stoichiometries of Ge-added  $\text{TiO}_2$  for NC6 and NC7 are the same, as has already been noticed by the XRD experiments. Moreover, a new Raman band appears at around the wavenumber of  $300 \text{ cm}^{-1}$  in the spectra of both NC6 and NC7. In fact, that Raman band corresponds to Ge nanodots [27]. A careful observation reveals that the specific Raman band becomes sharper for NC7 than for NC6. It sharpens even more for NC8. This indicates that the size of Ge nanodots gradually increases from NC6 to NC8, which has been visualized in figure 1, and also realized from the analysis of figure 2. Additionally, figures 1 and 2 have shown the abundant presence of Ge in NC8. The Raman experiments also support that fact. The Raman spectrum of NC8 almost looks like that of Ge; no Raman band of either  $\text{TiO}_2$  or Ge-added  $\text{TiO}_2$  is found. In sum, the Raman experiments totally corroborate the TEM and XRD studies, and depict a clear presentation of the morphology of  $\text{TiO}_2$ -Ge films.



**Figure 3.** HAADF images along with the elemental mappings of Ti, O and Ge for (a) NC5: sputtered from C5 (Ge = 5 wt%) and (b) NC8: sputtered from C8 (Ge = 33 wt%), respectively.

### 3.2. Optoelectronic properties

The preceding section shows that the morphology of  $\text{TiO}_2$ -Ge can be tailored in a wide range. We know that the physical properties, such as optical properties, electrical properties and thermoelectric properties, etc., of a material are greatly influenced by its structural properties. Hence, the extensive varieties of the structural properties of  $\text{TiO}_2$ -Ge are encouraging for obtaining a novel material for optoelectronic application, and the optoelectronic properties of  $\text{TiO}_2$ -Ge films are studied widely. Figure 6(a) presents the normalized

absorption coefficient ( $\alpha$ ) spectra of different  $\text{TiO}_2$ -Ge films along with that of  $\text{TiO}_2$ . Instead of  $\alpha$  spectra, the normalized  $\alpha$  spectra are plotted, because the values of absorption coefficients beyond the optical edges for Ge and  $\text{TiO}_2$  are widely varied. The absorption coefficients of Ge beyond the absorption edge are  $10^3 \text{ cm}^{-1}$  and higher [28], whereas the values for  $\text{TiO}_2$  are  $10^7 \text{ cm}^{-1}$  and higher [29]. For the present  $\text{TiO}_2$ -Ge samples,  $\alpha$  values beyond the optical edges range from  $10^3$  to  $10^7 \text{ cm}^{-1}$  depending on the Ge concentrations of the films. If the absorption coefficients spectra having huge differences of  $\alpha$  values are plotted together, the spectra having

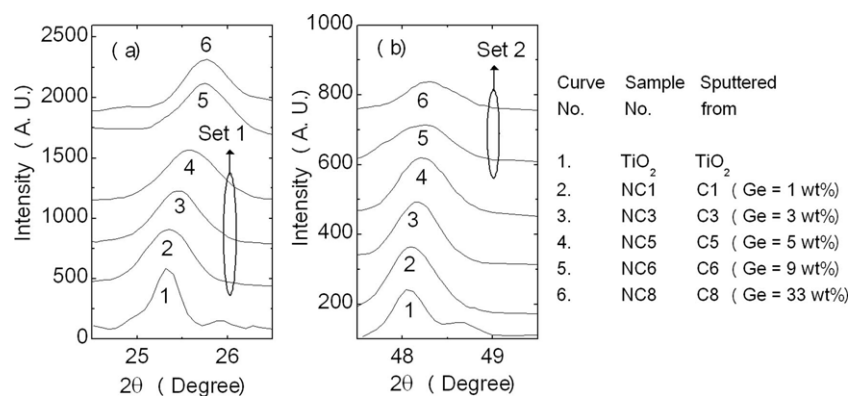


Figure 4. Comparison of TiO<sub>2</sub> anatase (a) (101) and (b) (200) XRD peaks.

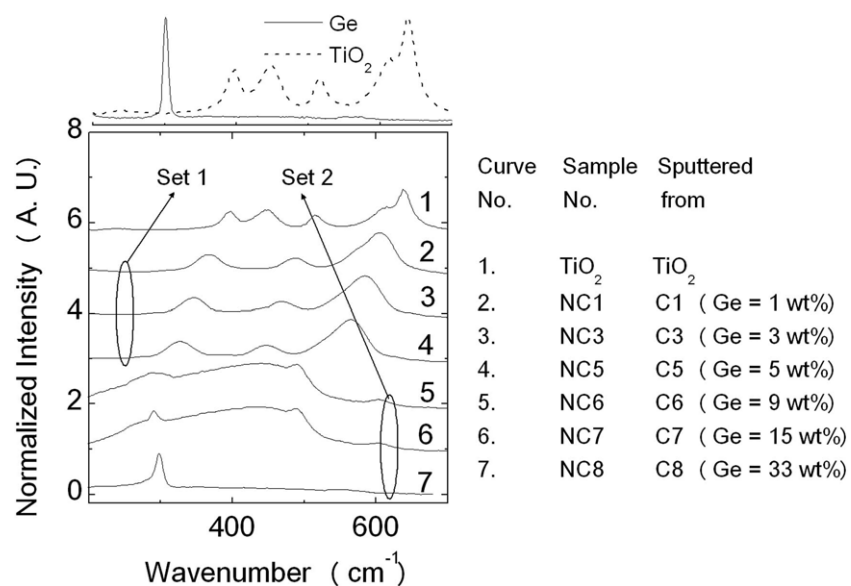
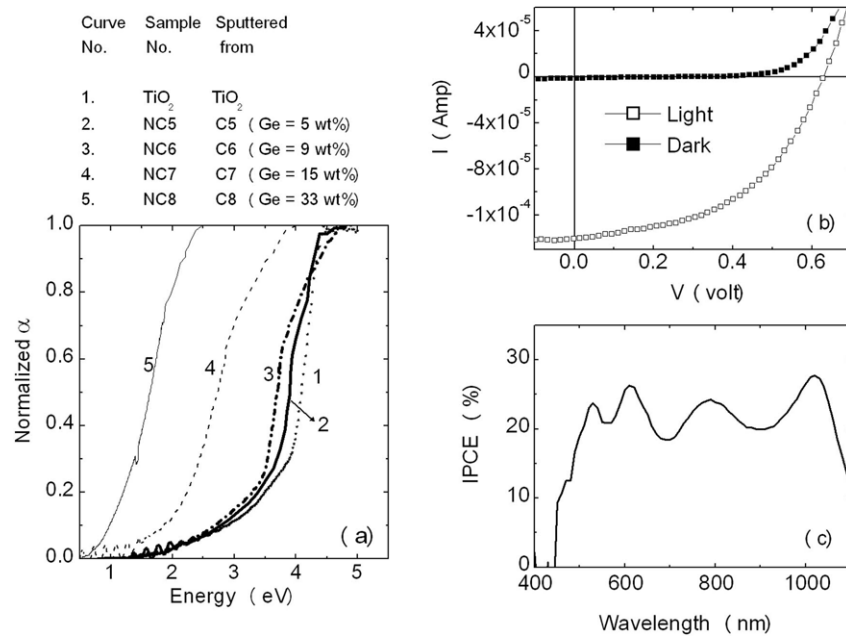


Figure 5. (a) Raman shift spectra of TiO<sub>2</sub>-Ge films. (b) Ideal Raman scatterings for Ge and TiO<sub>2</sub>.

lower  $\alpha$  values are very close to the abscissa (energy) axis. It even becomes difficult to differentiate these spectra from the energy axis. Hence, making the absorption edge of each film legible, the normalized absorption coefficient ( $\alpha$ ) spectra are drawn in figure 6(a) instead of simply the  $\alpha$  spectra. As observed in figure 6(a), the normalized  $\alpha$  spectra of TiO<sub>2</sub> and NC5 are very close. This means that the Ge association into the TiO<sub>2</sub> lattice does change the optical edge; however, that change is very small. The red shift of the absorption edge becomes significant for NC6 in which Ge nanodots are grown in the Ge-added TiO<sub>2</sub> matrix. The further red shifting of the optical edge is observed for NC7 and NC8. It was noticed earlier that the Ge nanodots of NC7 are bigger than those of NC6, and smaller than those of NC8. So, the tailoring of the optical gap of TiO<sub>2</sub>-Ge films could be correlated with the size modification of Ge nanodots. Actually, the optical gap of bulk Ge is 0.67 eV [28], situated in the infrared region of solar spectrum, and the quantum Bohr radius [30, 31] of Ge is 24.3 nm [32, 33]. If the size of Ge dots could be altered in the range of 24.3–0 nm, its band gap would be tailored from the

infrared to ultraviolet via visible energy due to the 3D quantum confinement effect [30–33]. That is why the size manipulation of Ge nanodots results in the variation of optical gap from the ultraviolet to infrared energy of TiO<sub>2</sub>-Ge films.

The electronic properties of wide-ranging optically active TiO<sub>2</sub>-Ge were studied. Table 1 displays the conductivities of TiO<sub>2</sub>-Ge films. The information presented in table 1 is really exciting. The dark conductivities ( $\sigma_D$ ) of TiO<sub>2</sub>-Ge films can be tailored over nine orders of magnitude. Actually, the concentration of Ge plays the main role in making the TiO<sub>2</sub>-Ge films conductive, since TiO<sub>2</sub> is almost an insulator ( $\sigma_D = 1.00 \times 10^{-12} \text{ S cm}^{-1}$ ). For the set 1 films (NC1–NC5), Ge addition (doping) in the TiO<sub>2</sub> lattice can change the lattice dynamics and electronic structure of TiO<sub>2</sub> in such a way that boosts the electronic transport. Hence, all the transport properties (dark conductivity ( $\sigma_D$ ), photoconductivity ( $\sigma_{Ph}$ ), photosensitivity ( $\sigma_{Ph}/\sigma_D$ )) improve with increasing Ge concentration (see table 1). This suggests that the Ge dopant states act as shallow traps [34] situated near to the conduction band and/or valence band. Those traps increase the charge



**Figure 6.** (a) Optical absorption spectra of TiO<sub>2</sub>-Ge films. (b) Dark and light (under AM1.5 solar radiation of 100 mW cm<sup>-2</sup>) current-voltage (*I*-*V*) curves of p-Si/TiO<sub>2</sub>-Ge (NC7: 0.5 μm thick) heterojunction solar cell. (c) IPCE spectrum of p-Si/TiO<sub>2</sub>-Ge (NC7: 0.5 μm thick) heterojunction solar cell.

**Table 1.** Thermal conductivity and electrical conductivity of TiO<sub>2</sub>-Ge nanocomposite superlattices.

| Sample           | Wt% of Ge in composite sputtering targets | Size of Ge dots in TiO <sub>2</sub> matrix (nm) | Dark conductivity (σ <sub>D</sub> ) (S cm <sup>-1</sup> ) | Thermal conductivity ( <i>k</i> ) (W cm <sup>-1</sup> K <sup>-1</sup> ) |                               |                                             |                                      |
|------------------|-------------------------------------------|-------------------------------------------------|-----------------------------------------------------------|-------------------------------------------------------------------------|-------------------------------|---------------------------------------------|--------------------------------------|
|                  |                                           |                                                 |                                                           | Photo response (σ <sub>Ph</sub> /σ <sub>D</sub> )                       | Ge as reference ( <i>k</i> 1) | TiO <sub>2</sub> as reference ( <i>k</i> 2) | Average ( <i>k</i> 1 + <i>k</i> 2)/2 |
| NC8              | 33                                        | >17                                             | 1.62 × 10 <sup>-02</sup>                                  | 1.14                                                                    | 0.088                         | 0.092                                       | 0.090                                |
| NC7              | 15                                        | 15                                              | 2.86 × 10 <sup>-03</sup>                                  | 2.32                                                                    | 0.037                         | 0.044                                       | 0.041                                |
| NC6              | 9                                         | 7                                               | 1.12 × 10 <sup>-05</sup>                                  | 4.61                                                                    | 0.008                         | 0.013                                       | 0.011                                |
| NC5              | 5                                         | —                                               | 3.78 × 10 <sup>-07</sup>                                  | 2.68                                                                    | 0.108                         | 0.116                                       | 0.112                                |
| NC3              | 3                                         | —                                               | 6.16 × 10 <sup>-09</sup>                                  | 1.45                                                                    | 0.114                         | 0.120                                       | 0.117                                |
| NC1              | 1                                         | —                                               | 3.31 × 10 <sup>-11</sup>                                  | 0.45                                                                    | 0.105                         | 0.115                                       | 0.110                                |
| TiO <sub>2</sub> | —                                         | —                                               | 1.00 × 10 <sup>-12</sup>                                  | —                                                                       | 0.11                          | —                                           | —                                    |
| Ge               | —                                         | —                                               | 1.45 × 10 <sup>-02</sup>                                  | —                                                                       | 0.58                          | —                                           | —                                    |

separation efficiency and the lifetime of charge carriers by charge carrier trapping; they improve light absorption and change the photoactivity [34–36]. Then afterwards, when the Ge nanodots are formed in the set 2 samples, the carrier transport process becomes a complex phenomenon. More mechanisms, like charge carrier activation to the mobility edges of Ge nanocrystals, tunneling of carriers between the neighboring Ge dots in the TiO<sub>2</sub> matrix and polaron hopping in the TiO<sub>2</sub> matrix, are added to the priory stated charge transport mechanism. As a result, the conductivities and photosensitivities are improved further, and TiO<sub>2</sub>-Ge becomes a next generation photovoltaic semiconductor. To ensure the photovoltaic quality of TiO<sub>2</sub>-Ge, p-Si/TiO<sub>2</sub>-Ge heterojunction solar cells were fabricated with a device structure of Al/p-Si/TiO<sub>2</sub>-Ge/ITO. Figures 6(b) and (c) display the photovoltaic properties, namely *I*-*V* characteristic and external quantum efficiency (IPCE) spectrum, of a heterojunction solar cell using NC7 of 0.5 μm thickness.

The preliminary properties of the heterojunction solar cell are encouraging for the further development of TiO<sub>2</sub>-Ge nanocomposite solar cells.

### 3.3. Thermoelectric properties

The nanostructured pattern of photovoltaic grade TiO<sub>2</sub>-Ge materials is inspiring to study their thermoelectric properties. Recent studies show that nanostructured semiconductors, such as the Si/Ge superlattice [6–8] and Ge dots in SiO<sub>2</sub> [9, 10], are superior systems for thermoelectric applications, because their confined low-dimensional structures block the phonons and transmit the electrons. If TiO<sub>2</sub>-Ge nanocomposite were to become a thermoelectric semiconductor, it will be to our advantage to generate electricity by photoelectric and thermoelectric conversion, simultaneously. Commonly, the thermoelectric quality of a semiconductor is judged by the thermoelectric figure-of-merit,  $ZT = S^2 \sigma_D T / k$ ,



where  $\sigma_D$  is electrical conductivity,  $S$  is the thermopower or Seebeck coefficient (it is related to  $\sigma_D$  as  $S = (\pi^2 k_B^2 T / 3e) (\partial \ln \sigma_D / \partial E)_{E_F}$  for semiconductors [37]),  $k$  is the thermal conductivity and  $T$  is the absolute temperature. A semiconductor should have high  $\sigma_D$  and low  $k$  to be a good thermoelectric material. It has already been evident that the TiO<sub>2</sub>-Ge films have a promising  $\sigma_D$ s. Now the  $k$  values of TiO<sub>2</sub>-Ge nanocomposites have to be checked. Table 1 demonstrates the  $k$  values of TiO<sub>2</sub>-Ge films. It is exciting that the thermal conductivities of NC6, NC7 and NC8 are lower than that of TiO<sub>2</sub>. The introduction of Ge dots in the TiO<sub>2</sub> matrix creates a macroscopically inhomogeneous superlattice structure which enhances phonon scattering, and resultantly decreases the  $k$  values of TiO<sub>2</sub>-Ge films. Moreover, when the Ge dots are smaller than the quantum Bohr radius of Ge, they confine phonons [38] or even strongly scatter phonons [39], which results in a further reduction of thermal conductivity. Therefore, the thermal conductivities of TiO<sub>2</sub>-Ge nanocomposites could be tailored by varying the size of the Ge nanodots.

#### 4. Conclusion

In conclusion, a nanocomposite semiconductor TiO<sub>2</sub>-Ge which includes Ge nanodots in the matrix of Ge-added TiO<sub>2</sub> has been developed. The novelty of this nanocomposite semiconductor is that its morphology could be tailored in a wide range. As a consequence, extensive variations of photoelectric and thermoelectric properties have been achieved for TiO<sub>2</sub>-Ge. The promising properties suggest that this nanocomposite material is an ideal next generation semiconductor for photovoltaic, thermoelectric and photo-thermo-electric applications.

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