Single-Phase Anatase Structure and Dominant Metallic Ge in Ge/TiO₂ Multi-Layer Films Using a Differential Pumping Co-Sputtering System

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Abstract

This study investigates the preparation of Ge/TiO₂ multi-layer films using a differential-pumping co-sputtering system (DPCS). This system has two chambers with different atmospheres, pure Ar for the Ge target and 0.5 %O₂ in Ar for the TiO₂ ceramic target. The optical absorption spectra of the multi-layer films obviously shift to visible and near-infrared regions with increasing Ge layer thickness, while keeping O/Ti composition ratios of 2.3±0.1 in TiO₂. X-ray diffraction results indicate that the TiO₂ layer forms a single-phase anatase structure in the multi-layer films. X-ray photoelectron spectroscopy also indicates that metallic Ge is dominant in the multi-layer film with negligible Ge-oxide. Therefore, DPCS provides a multi-layer film with a single-phase anatase structure in the TiO₂ layer and a dominant metallic element in the Ge layer.

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Introduction

Quantum-dot solar cells have attracted much attention because of their potential to increase conversion efficiency [1]. Specifically, the optical absorption edge of a semiconductor nanocrystal often shifts due to quantum size effects. The optical band gap can thus be tuned to an effective energy region in order to absorb the maximum intensity of the solar radiation spectrum. Furthermore, quantum dots produce multiple electron-hole pairs per photon through impact ionization, whereas a bulk semiconductor produces one electron-hole pair per photon.

A wide-gap semiconductor sensitized by semiconductor nanocrystals is a candidate material for such use. Wide-gap materials such as TiO_2 and ZnO can absorb only the ultraviolet (UV) part of the solar radiation spectrum. The semiconductor nanocrystal supports the absorption of visible (vis) and near-infrared (NIR) light. Various nanocrystalline materials (InP [2], CdSe [3], CdS [4, 5], PbS [6], and Ge [7, 8]) have been investigated as sensitizers for TiO_2 . Wide-gap semiconductor ZnO was also investigated, since the band gap and the energetic position of the valence band maximum and conduction band minimum of ZnO are very close to those of TiO_2 [9]. Most of these composite materials were synthesized through chemical techniques, although physical deposition (e. g., sputtering) is also useful. In addition, one-step synthesis of a composite thin film is favorable for low-cost production of solar cells. Package synthesis requires a specific material design for each deposition technique (e.g., RF sputtering [10, 11] and hot-wall deposition [12]). In our previous study [8], an anatase-dominant structure in the TiO_2 matrix and vis-NIR absorption in Ge nanocrystals were exhibited in Ge -added TiO_2 (Ge/TiO_2) nanocomposite film, prepared by RF sputtering with a composite target made from ceramic TiO_2 with Ge chips. The TiO_2 matrix contained a small amount of rutile structure, although the anatase structure is favorable for the matrix because carrier mobility and photoconductivity in the anatase structure exceed those in the rutile structure [13]. A pure anatase structure formed at relatively high oxygen content exceeding 0.5 % in Ar, but Ge was fully oxidized [8]. Hence, it is quite difficult to retain both the single-phase anatase structure in TiO_2 and

the pure element in Ge simultaneously when using package synthesis with the composite target. The present study focuses on the use of a differential-pumping co-sputtering system (DPCS) [14]. Specifically, this system contains two chambers that, when evacuated individually, are capable of supplying different atmospheres. The two chambers are separated horizontally by a center-wall with a perpendicular clearance of 1-2 mm between the center-wall and the substrate holder to restrict a cross-contamination between the two chambers. Hence, this system can provide desirable atmospheres of Ar with diluted oxygen for the TiO_2 target and pure Ar for the Ge target. A Ge/ TiO_2 multi-layer can be prepared by rotating the substrate with negligible cross-contamination. In these atmospheres, a Ge/ TiO_2 thin film may simultaneously form a single-phase anatase structure in TiO_2 and a pure metallic element in Ge. As the first step for preparing a nanocomposite film containing Ge nanocrystals embedded in the TiO_2 matrix, a multi-layer structure (i.e., a multi-quantum well structure) is employed here to simplify a heterogeneous Ge- TiO_2 system. In the present study, we use DPCS to investigate a preparation of Ge/ TiO_2 multi-layer film with a single-phase anatase structure in the TiO_2 layer and a pure metallic element in the Ge layer.

Experimental details

A Ge/ TiO_2 multi-layer film was prepared by DPCS, with a 7.62 cm (3 inch) diameter ceramic TiO_2 target with 4N pure (Kojundo Chemical Laboratory, Saitama, Japan) in an atmosphere of 0.5 % O_2 in Ar and a Ge target in Ar with 6N pure. Each chamber has a pumping system consisting of a mechanical pump and a turbomolecular pump (1000 L/s), achieving a vacuum of 2.5×10^{-4} Pa. The total gas pressure of Ar and 0.5 % O_2 in Ar was fixed at 0.20 Pa for the Ge target and at 0.26 Pa for the TiO_2 target. Ge/ TiO_2 multi-layer films were deposited on a Corning #7059 glass substrate that rotates with negligible cross-contamination between the two chambers. RF power was kept constant at 200 W for the TiO_2 target and at 30 W for the Ge target, to prepare layer structures with thicknesses of 2 nm, 5 nm, 10 nm, and 15 nm for the Ge layer and 34 nm in the TiO_2 layers. In

these layer structures, TiO_2 is employed for both the top and the bottom layers. The total thickness of the Ge/TiO_2 thin films is kept constant at 2 μm in the present study. The substrate temperature was kept constant at RT with no RF bias. The Ge/TiO_2 multi-layer films thus deposited were successively annealed at 873 K for 60 min in Ar to crystallize Ge and TiO_2 . The film was structurally characterized using X-ray diffraction (XRD) with $\text{Cu-K}\alpha$ radiation (Philips X'pert system, PANalytical, Almelo, The Netherlands). A grazing angle configuration was used. The optical absorption spectrum of the film was measured using UV-vis-NIR spectroscopy (Shimadzu UV3150, Kyoto, Japan), and the composition of the film was analyzed using energy-dispersion spectroscopy (EDS) (EDAX Phoenix, NJ, USA), operating at 10 kV with standard samples of MnTiO_3 to calibrate the analyzed results for element Ti, and with $\text{Bi}_3\text{Ge}_4\text{O}_{12}$ for elements Ge and oxygen. The nanoscale structure was observed using transmission electron microscopy (TEM) (TOPCON, EM-002B, Tokyo, Japan) operating at 200 kV and high-resolution transmission electron microscopy (HRTEM) (Hitachi H-9000NAR, Hitachi, Ltd., Tokyo, Japan) operating at 300 kV. TEM samples were prepared using a focused ion beam system (Hitachi, FIB2100, Tokyo, Japan) with Ga^+ ion in the range of 10-40 kV. The chemical bonding state of the films was measured using X-ray photo electron spectroscopy (XPS) (Thermo Scientific, ESCALAB 250Xi, MA, USA) with $\text{Al-K}\alpha$ radiation. Sample surface was sputter-etched by Ar^+ ion beam for 1080 s with a power of 10 W to reach a Ge layer. The peaks were referenced to the C1s peak at 284.6 eV for charge correction.

Results and discussion

Figure 1a presents a typical cross-section TEM image of as-deposited amorphous film with a 10 nm-thick Ge layer. The designed layer structure is clearly seen as a modulation of contrast. Depending on deposition rates, bright stripes correspond to Ge, and the dark area corresponds to TiO_2 . Each layer thickness thus observed corresponds well to the deposition rates. Fig. 1b presents a TEM image of the sample annealed at 873 K for 60 min. Slightly bright and dark areas are seen in

the Ge layer as indicated by circles with the label c and d. The selected-area electron diffraction (SAED) patterns of the areas (c and d) are presented in Fig. 1c and d. These areas contain Ge and TiO₂ with anatase structure. HRTEM image of the same sample is also presented in Fig. 1e. The hetero-interface between the TiO₂ and Ge is clearly seen with a designed Ge layer of 10 nm thick. Therefore, interdiffusion between the Ge layer and the TiO₂ layer seems to be negligible during the postannealing at 873 K for 60 min. The Ge/TiO₂ thin film therefore forms a multi-layer structure. The present study employs thicknesses from 2 nm to 15 nm in the Ge layer while keeping 34 nm in the TiO₂ layer.

Figure 2 depicts the transmittance spectra of Ge/TiO₂ multi-layer films annealed at 873 K for 60 min. For comparison, the transmittance of the TiO₂ prepared in pure Ar is also presented [15]. With no Ge layer, an optical absorption edge of TiO₂ is observed at 400 nm, with relatively high transparency in a wide range from UV to NIR, in contrast with low transparency in the TiO₂ prepared in pure Ar [15]. This low transparency is due to an oxygen deficit from stoichiometry in TiO₂ with a composition ratio O/Ti of 1.9, in contrast with excess oxygen with 2.2 in the present study. An atmosphere of 0.5 %O₂ in Ar therefore improves the optical transparency in TiO₂. In addition, the optical absorption edge shifts toward the longer wavelength region as the Ge-layer thickness increases, while maintaining transparency with a composition ratio O/Ti of 2.3±0.1. This result indicates that DPCS provides a sufficient inclusion of oxygen, in both pure TiO₂ thin film and in TiO₂ layers in the multi-layer films.

Figure 3a plots a typical XRD pattern of as-deposited Ge/TiO₂ multi-layer films. With no Ge layer, rutile structure with broad diffraction peak is formed in TiO₂ film, while the Ge/TiO₂ film with a 10 nm-thick Ge layer provides amorphous structure. Postannealing crystallizes both the Ge and the TiO₂ layer. Figure 3b plots a typical XRD pattern of Ge/TiO₂ multi-layer films annealed at 873 K for 60 min. With no Ge layer, a phase mixture of anatase and rutile structure is formed in TiO₂ film. A 2 nm-thick Ge layer reduces the peak intensity of the rutile structure. The Ge peak

appears at thicknesses exceeding 5 nm, and the rutile structure disappears. Hence, a layer structure with crystalized Ge and a single-phase anatase structure in TiO₂ are formed at thicknesses exceeding 5 nm. This result is in good agreement with the SAED results (Figs. 1c and d). The disappearance of the rutile structure in the multi-layer films is probably responsible for increasing the O/Ti composition ratio from 2.2 in pure TiO₂ film to 2.4 in 10 nm-thick, for instance, since a relatively high oxygen ratio exceeding 0.5 %O₂ in Ar in a pure TiO₂ excludes rutile structures (i.e., single-phase anatase structures) [8]. Similar results were also seen in the Ge/TiO₂ nanocomposite film prepared with a composite target made from ceramic TiO₂ with Ge chips [8]; however, a slight rutile structure remained due to an insufficient supply of 0.3 %O₂ in Ar, which prevented fully oxidizing Ge. The results in Figs. 2 and 3 therefore indicate that DPCS provides TiO₂ with a single-phase anatase structure, which is favorable for solar cells, in Ge/TiO₂ multi-layer films with an appropriate O/Ti composition ratio of 2.3 ± 0.1 .

Figure 4 plots a typical optical absorption spectrum of Ge/TiO₂ multi-layer film with a 10 nm-thick Ge layer, which corresponds to a Ge concentration of 8.8 at.% in the entire multi-layer film, according to EDS analysis. For comparison, absorption spectra of the TiO₂ film and the Ge/TiO₂ nanocomposite film containing a similar concentration of 8.7 at.% Ge [8] on EDS analysis are presented in the figure. The absorption edge in the TiO₂ appears in the UV range, while both the multi-layer film and the nanocomposite film exhibit an obvious shift to the vis-NIR range, indicating that they absorb a desirable energy region for high conversion efficiency [16]. The optical absorption shift in the nanocomposite film (8.7 at.% Ge) was induced by the quantum size effects of Ge nanocrystals embedded in the TiO₂ matrix [8]. In addition, the inclination of the optical absorption edge in the multi-layer film (8.8 at.% Ge) exceeds that in the nanocomposite film (8.7 at.% Ge), although onset absorption is almost the same. This difference is due to the size distribution of Ge. Specifically, the size of Ge nanocrystals in the nanocomposite film (8.7 at.% Ge) was distributed broadly from 0.5 nm to 8 nm in radius, according to the result of small-angle X-ray diffraction

spectroscopy, whereas the thickness of the Ge layer remained constant at 10 nm in the multi-layer film (Figs. 1b and e). In addition, nanocomposite film (8.7 at.%Ge) was prepared with a composite target made from ceramic TiO₂ with Ge chips in an oxygen atmosphere of 0.3 % in Ar, in which metallic Ge was partially oxidized and quantum size effects became weak. In contrast, DPCS can reduce the oxidation of Ge by employing a pure Ar atmosphere for the Ge target.

The XPS spectrum of Ge/TiO₂ multi-layer film with a 10 nm-thick Ge layer is plotted in Fig. 5. The dotted lines indicate peak positions of Ge(0)3d, Ge(IV)3d, O(II)2s, Ti(IV)3p, and Ti(0)3p. The spectrum has three peaks of Ge(0)3d at 29.3 eV, which corresponds to metallic Ge [17], with relatively strong intensity, O(II)2s at 22.4 eV, which corresponds to Ti-oxide such as TiO₂ compound, and a broad peak consisting of Ti(IV)3p at 37.3 eV [18, 19], which also corresponds to TiO₂ compound, and Ge(IV)3d [17], which corresponds to Ge-oxide such as GeO₂ at 32.5eV with no obvious peak intensity. Ti(0)3p, which corresponds to metallic Ti, is also located at 32.5 eV [20], but metallic Ti is probably oxidized fully in the multi-layer film due to a sufficient supply of the oxygen in the sputtering atmosphere and no diffraction peak of metallic Ti in the SAED and XRD result (Figs. 1 and 3). The composition ratio O/Ti is estimated to be 2.4, using the peak areas of Ti(IV)3p and O(II)2s. This ratio is in good agreement with the EDS-analysis result. Thus, damage induced in the sample is negligible during XPS analysis with a sputtering power of 10 W in Ar. A dominant peak of metallic Ge in the spectrum thus indicates negligible oxidation in the Ge layer. This result strongly suggests that inclusion of metallic element Ge in the multi-layer film exceeds that in the nanocomposite film, although analyzed Ge is almost the same in both films. It is therefore concluded that DPCS provides a dominant metallic element in the Ge layer by employing pure Ar for the Ge target with negligible cross-contamination of oxygen from the adjacent chamber with 0.5 %O₂ in Ar for the ceramic TiO₂ target.

Using basic quantum theory for confined electrons in a square well of finite depth, the following equation can be derived for the lowest-order solution of the wave function [21]: $COS(kL/2) =$

k/Q , where $k = 2\pi(2m^*\Delta)^{1/2}/h$ and $Q = 2\pi(2m^*V)^{1/2}/h$. Here, Δ is the increase of electron energy from the ground state to its first bound state when confined in a quantum well with depth V and width L , m^* is the effective mass of an electron-hole pair, and h the Planck constant. The above equation assumes that the coupling between wave functions in adjacent wells is negligible. Using $m^* = 0.028m_0$ [22] and $V = 1.27$ eV, which is assumed to be half the difference in band gaps of Ge (0.66 eV) and TiO_2 (3.2 eV), the optical gap of the Ge/ TiO_2 multi-layer film with a 10 nm-thick Ge layer is calculated to be 0.75 eV, which is nearly the same as the onset absorption of the experiment result (Fig. 4). Therefore, the optical absorption shift in the multi-layer film is obviously due to quantum size effects in the Ge layer.

The annealing atmosphere also causes oxidation of Ge in Ge/ TiO_2 multi-layer film. A similar multi-layer film with a 10 nm-thick Ge layer and a 22 nm-thick TiO_2 layer and prepared by evaporating TiO_2 powder with an electron beam and Ge powder with thermal heating exhibited a blue shift in the optical absorption edge during postannealing in air at temperatures exceeding 573 K [23]. This result indicated that the Ge layer was completely oxidized and that quantum size effects disappeared, although the TiO_2 layer formed a single-phase anatase structure. In contrast, annealing in the Ar atmosphere employed here provides negligible oxidation of Ge (Fig. 5) and a single-phase anatase structure (Fig. 3b). It should be noted that oxidation of Ge in the Ge- TiO_2 heterojunction is also negligible during postannealing (Figs. 1e and 5), since TiO_2 has less free energy of reaction and is thermodynamically more stable than GeO_2 [24].

From the optical and structural results, we conclude that DPCS provides a multi-layer film with a dominant metallic element in the Ge layer and single-phase anatase structure in the TiO_2 layer with O/Ti composition ratios of 2.3 ± 0.1 in the multi-layer films, which exhibits vis-NIR absorption due to quantum size effects in the Ge layer. Our next task is to prepare a composite film with Ge nanocrystals embedded in the TiO_2 matrix by DPCS for quantum-dot solar cells. The alternative to a step deposition of each layer (Ge and TiO_2) employed in the present study, a tandem deposition

with continuously rapid rotation of a substrate, may be favorable for preparing such composite films, since tandem deposition provides a similar composite film with magnetic metal nanocrystals embedded in an oxide matrix [25].

Conclusions

DPCS has been employed to prepare Ge/TiO₂ multi-layer films. It should be pointed out that the TiO₂ layer forms a single-phase anatase structure with an O/Ti composition ratio of 2.3 ± 0.1 in these films. The optical absorption edge shifts toward the vis-NIR ranges, favorably absorbing a desirable energy region for high conversion efficiency. An XPS spectrum indicates that metallic Ge is dominant in the 10 nm-thick Ge layer with negligible Ge-oxide. Therefore, this system provides an Ge/TiO₂ multi-layer film with a single-phase anatase structure in the TiO₂ layer and a dominant metallic element in the Ge layer.

Acknowledgments

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Figure Captions

Fig. 1. Cross-section TEM image and SAED pattern of Ge/TiO₂ multi-layer film with a 10 nm-thick Ge layer. (a) As-deposited image. (b) Annealed image. (c) SAED pattern. (d) HRTEM image.

Fig. 2. Optical transmittance spectra of Ge/TiO₂ multi-layer films annealed at 873 K for 60 min. For comparison, the optical transmittance spectrum of TiO₂ thin film prepared in a pure Ar is also presented [15].

Fig. 3. XRD pattern of Ge/TiO₂ multi-layer films with different Ge layer thicknesses. (a) As-deposited pattern. (b) Annealed pattern. Black dots indicate TiO₂ with an anatase structure, circles indicate TiO₂ with a rutile structure, and red dots indicate Ge.

Fig. 4. Typical optical absorption spectrum of Ge/TiO₂ multi-layer film with a 10 nm-thick Ge layer. For comparison, the optical absorption spectra of TiO₂ thin film and Ge/TiO₂ nano-composite film are also presented [8].

Fig. 5. XPS spectrum of Ge/TiO₂ multi-layer film with a 10 nm-thick Ge layer.

Fig-1

Fig-2

Fig-3

Fig-4

Fig-5