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THE ANALYSIS OF STRUCTURE FOR THE MULTI-LAYERED OF Ge/TiO_2 FILMS PREPARED BY THE DIFFERENTIAL PRRESSURE CO-SPUTTERING

ANALIZA STRUKTURY WIELOWARSTWOWYCH FILMÓW Ge/TiO_2 WYTWARZANYCH METODĄ RÓŻNICOWO-CIŚNIENIOWEGO WSPÓŁROZPYLANIA JONOWEGO

We tried to fabricate the Ge/TiO_2 composite films with the differential pressure (pumping) co-sputtering (DPCS) apparatus in order to improve the optical properties. In the study, the micro structure of these thin films has been evaluated. TEM image revealed that the thin film was alternately layered with TiO_2 and Ge, lattice fringes were observed both of Ge layer and TiO_2 layer. There were portions that lattice fringe of Ge was disturbed near the interface of Ge and TiO_2. X-ray photoelectron spectroscopy elucidated that there were few germanium oxides and a part with the thin film after annealed.

Keywords: TiO_2, Ge, solar cells, sputtering

W pracy przedstawiono rezultaty badań mających na celu wytworzenie warstw kompozytowych Ge/TiO_2 wykorzystując aparaturę do różnicowo-ciśnieniowego współrozpylania jonowego (DPCS) w celu poprawy właściwości optycznych. Mikrostruktura warstw została zbadana z zastosowaniem mikroskopii TEM. Analiza TEM wykazała, że cienki film składał się z naprzemiennie ułożonych warstw TiO_2 oraz Ge, a dodatkowo zlokalizowano krawędzie sieci przestrzennych Ge i TiO_2. Rentgenowska spektroskopia fotoelektronów wykazała niewielkie ilości tlenków germanu oraz występowanie cienkiego filmu po procesie wyżarzania.

1. Introduction

Nowadays, the primary solar cell technology is silicon cell, which conversion efficiency has reached to a practical limit of 25% (the theoretical limit is 29%). In order to achieve higher conversion ratio of sunlight into electricity, quantum dots (QDs) solar cells have attracted much attention. As a candidate of the novel materials for the QDs solar cell, a composite film of anatase-dominant TiO_2 sensitized by Ge nanocrystal (Ge/TiO_2) was presented by S. Abe et al [1]. In their study, the Ge/TiO_2 films were prepared by an r.f. reactive sputtering using a composite target of a Ge chip set on a TiO_2 disk under a mixed gas atmosphere of argon and oxygen. However, it is difficult for a conventional sputtering apparatus having one chamber to provide sufficient performance to the composite film, because the optimum deposition condition of Ge and TiO_2 should be different each other. Recently, the differential pressure (pumping) co-sputtering system (DPCS) [2], which can co-deposit each material under different atmosphere, was developed. In this study, we tried to fabricate the Ge/TiO_2 composite films with the DPCS in order to improve the optical properties of the film [3].

2. Experimental procedure

The differential pressure (pumping) co-sputtering system (DPCS, ULVAC,RSSI-2T) having two chambers with a differential pumping system, was employed in this study. Both chambers were evacuated to a vacuum better than 4×10-4 Pa prior to deposition. Ge (99.999% in purity) target in the left chamber and TiO_2 (99.99% in purity) target in the right were sputtered in high purity Ar gas and in a mixture of argon and oxygen (oxygen content was fixed at 0.5 percent), respectively. Square coupons (25 mm×25 mm) of Alkali-free glass (Corning # 7059) and mirror-polished Si wafer were used as substrates. All the substrates were cleaned ultrasonically with acetone before sputtering deposition. Working pressure in the left (Ge) and the right chamber (TiO_2) were kept at 0.20Pa and 0.27Pa, respectively. Input power of r.f. (13.56MHz) for sputtering deposition was fixed at 30W or 200W for Ge or TiO_2, respectively. Sputtering deposition was performed by stepwise rotation of substrate holder without deliberate bias or heating application to the substrate to prepare nano-multilayered Ge/TiO_2 composite films. The different thickness of the Ge and TiO_2 layers was obtained by controlling open/close time of each shutter and input power to each target. The Ge/TiO_2

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composite films were successively post-annealed at 873 K for 60 min in Ar gas atmosphere to crystallize Ge and TiO_2 phase. TEM studies of cross sectional sample of the film were carried out with a TOPCON, EM-002B. The chemical bonding state of the films was measured using X-ray photo electron spectroscopy (XPS) (Thermo Scientific, ESCALAB 250Xi).

3. Results and discussion

Figure 1a shows the cross-section TEM image of 8.8 at.% Ge/TiO_2 with 10 nm-thick Ge layer annealed at 873 K for 60 min for crystallization. The selected-area electron diffraction (SAED) pattern of the area is presented Figure 1b. The Ge/TiO_2 thin film forms a multi-layer structure. From Figure 1a, irregular contrast occurs in the TiO_2 layer in the Ge for crystallization occurs by annealing. Furthermore the contrast in layer of Ge did not look like a quantum dot, but not a uniform layer, Ge phase seemed a collection of plate structure. The analysis of SAED figures, Ge phase and anatase phase in most cases, and some rutile phase was confirmed.

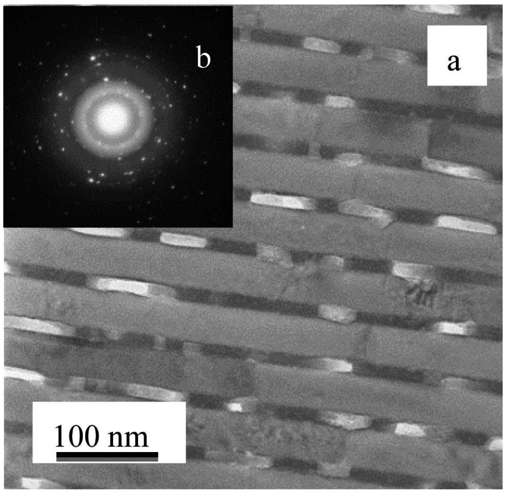

Fig. 1. Cross section TEM image and SAED pattern of Ge/TiO_2 multi-layer film

Figure 2 shows the XPS of 8.8 at.% Ge/TiO_2 multi-layer. The spectrum of as-deposited film has only one peak of Ge 3d at 29.3 eV [4, 5], and no other peak corresponding to Ge oxide was observed. On the other hand, the spectrum of annealed film has two broad peaks at 32.5 eV and 37.3 eV in addition to the main peak at 29.3eV. The broad peak at 32.5 eV [4, 5] and 37.5 eV [6] correspond to Ge oxide such as GeO_2, and Ti 3p, respectively. Even if oxidations of Ge were occurred in the thin film by annealing, it was very small.

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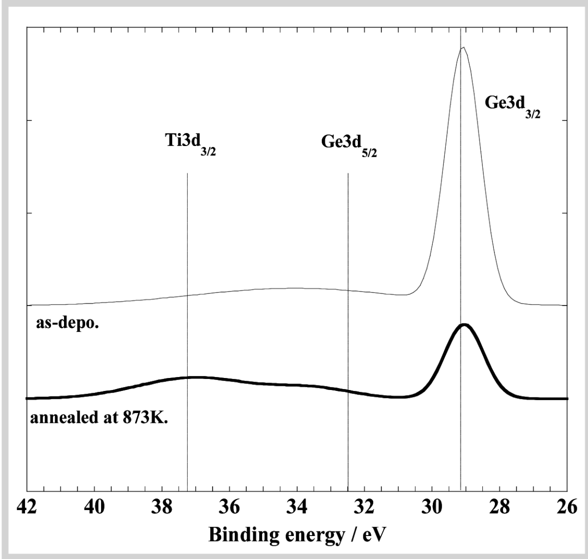

Fig. 2. XPS of 8.8 at.%Ge/TiO_2 multi-layered film

4. Conclusions

The multi-layered of Ge/TiO_2 films were prepared using the differential pumping co-sputtering system and following results were obtained. The Ge/TiO_2 composite films were successively post-annealed at 873 K for 60 min in Ar gas atmosphere to crystallize Ge and TiO_2 phase. TEM images and SAED patterns of the annealed multi-films of Ge/TiO_2 indicated that the Ge phase and anatase phase were dominant. Furthermore XPS spectrum indicated that metallic Ge is dominant in the films with negligible Ge-oxide.

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