Materials Letters 143 (2015) 80–83

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Structural variation and electrical properties of amorphous silicon ruthenium thin films embedded with nanocrystals

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ARTICLE INFO

Article history:
Received 17 November 2014
Accepted 9 December 2014
Available online 20 December 2014

Keywords:
a-$Si_{1-x}Ru_x$ thin film
Structural evolution
Resistivity
Nanocrystals

ABSTRACT

The structural variation and electrical properties in both as-deposited and annealed amorphous silicon ruthenium thin film are investigated. Results indicate that the introduced Ru atoms further degrade the amorphous network order and Ru_2Si nanocrystals are found in the as-deposited sample. The phase transformation of ruthenium silicide and the formation of Si nanocrystals are observed after annealing treatment. Significant resistivity reduction is obtained with the increase of Ru concentration. This material is a potential candidate for infrared detectors.

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1. Introduction

Amorphous silicon (a-Si) based thin film has been a technically important material for solar cells, thin film transistors, infrared detectors and lithium ion batteries [1–4]. However, the performance of a-Si based devices is strongly limited by the structural degradation caused by disordered amorphous network and defects. It is well known that the predesigned nanocrystals embedded amorphous silicon absorber layer exhibits higher conversion efficiency and can reduce light-induced metastability in Si tandem solar cells [5,6]. Moreover, the partially nanocrystalline Si thin film presents lower noise than the amorphous one [7], making itself a potential candidate for infrared thermal imaging devices. To achieve the nanocrystallization of amorphous silicon thin films, glow discharge of highly H_2-diluted silane (SiH_4) [8] or metal induced crystallization (MIC) [9,10] are technological approaches generally employed. It is noted that besides the effect of MIC, several unique photoelectrical properties obtained by introducing metal elements in a-Si thin films have stimulated enormous research interest in the literature [11–13]. It is reported that ruthenium (Ru) silicide has promising properties in band engineering among transition metal silicides. Filonov et al. [14] demonstrated Ru_2Si_3 to be a direct band gap semiconductor with energy gap of 0.41 eV by ab initio calculations while Lenssen et al. [15] found a band gap of 0.84 eV by experiments. In our early work [16], although a new paramagnetic center was found in hydrogenated amorphous silicon ruthenium (a-$Si_{1-x}Ru_x$:H) thin films, the crystallization of ruthenium silicides was not clearly clarified. In this paper, attempts are mainly focused on the structural evolution in both as-deposited and annealed amorphous silicon ruthenium (a-$Si_{1-x}Ru_x$) thin films. The electrical properties and mechanism are discussed as well.

2. Experimental procedure

The nanocrystals embedded a-$Si_{1-x}Ru_x$ thin films with a thickness of 400 nm were deposited by co-sputtering on c-Si substrates covered with SiO_2. Deposition condition was coincident with our early work [17], except that several Ru chips (99.95%) were fixed on the Si target (99.999%) and H_2 flow was not introduced here. The nominal Ru concentration, varying from 1% to 8%, was estimated by the target coverage proportion of Ru chips. Annealing treatment was carried out in a quartz tube in Ar atmosphere with a temperature range of 500–700 °C for 30 min. The vibrational modes of a-$Si_{1-x}Ru_x$ amorphous network were measured by RENISHAW inVia Raman Microscope at a wavelength of 514 nm. The power was set below 2 mW while the beam was defocused to a diameter of 2 μm to avoid laser-induced crystallization. X-ray diffraction spectra (XRD) were measured by PANalytical X'pert HighScore XRD instrument. To observe the nanocrystals embedded regions of a-$Si_{1-x}Ru_x$ thin films, high-resolution Transmission electron microscope (HRTEM) photographs were taken in an FEI Tecnai F20 field emission gun microscope. Resistivity and Temperature coefficient of resistivity (TCR) were measured by Keithley6517A semiconductor characterization system.

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http://dx.doi.org/10.1016/j.matlet.2014.12.045
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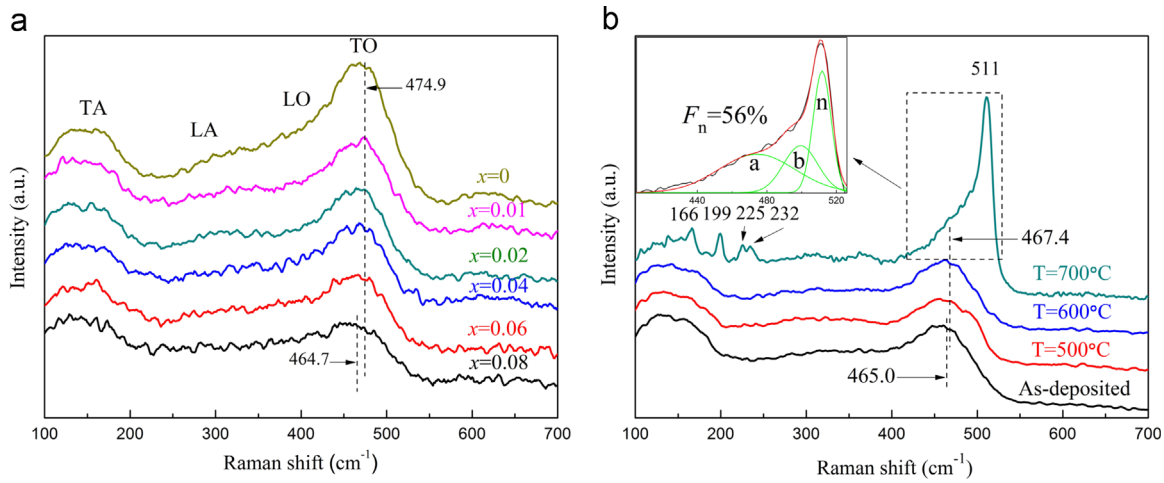

Fig. 1. Raman spectra of (a) as-deposited and (b) annealed a-$Si_{1-x}Ru_x$ thin films.

3. Results and discussions

The Raman spectra of as-deposited a-$Si_{1-x}Ru_x$ thin films are shown in Fig. 1(a). The position of transverse optical (TO) peak moves 10.2 cm^{-1} towards short wavenumber from 474.9 cm^{-1} to 464.7 cm^{-1} with the increase of nominal Ru concentration x from 0 to 0.08. Moreover, the TO linewidth (Γ_{TO}) increases from 60.5 cm^{-1} to 80.0 cm^{-1}. And the Si–Si bond-angle variation $\Delta\theta$, calculated from the linear relation: $\Gamma_{TO}=15+6\Delta\theta$, varies from 7.6° to 10.8°. The integrated intensity ratio I_{TA}/I_{TO} increases from 0.82 to 1.56 and I_{LA+LO}/I_{TO} increases from 1.06 to 1.47, respectively. These variations may be caused by different sizes and eletronegativities between Si and Ru atoms, revealing a greater disorder on short and medium ranges and a generation of more defects [18]. The results of annealed samples in the temperature range of 500–700 °C are presented in Fig. 1(b) with x fixed at 0.06. The position of TO peak moves slightly about 2.4 cm^{-1} from 465.0 cm^{-1} (deposited state) to 467.4 cm^{-1} (600 °C). This change can be regarded as an improvement of short-range order before crystallization [19]. Then the TO peak shifts to 511 cm^{-1} at 700 °C, which is a typical sign of nanocrystalline Si. The inset in Fig. 1(b) shows the deconvolution of this TO peak. The three Gaussian peaks labeled a, b, and n arise from the vibrations of amorphous silicon, grain boundaries and crystal grains, respectively. The Si crystalline volume fraction (F_n) including grain boundaries and crystal grains, is about 56% here. A series of small peaks centered at 166 cm^{-1}, 199 cm^{-1}, 225 cm^{-1} and 232 cm^{-1}, appears as well when annealing temperature rises to 700 °C. These peaks may come from the vibrations of the Ru–Si bonds, which are also noticed by Jelenkovic et al. [20].

The XRD spectra of the as-deposited samples with different nominal Ru concentrations exhibit no diffraction peaks, so they are not provided here. Fig. 2 shows the results of annealed samples in the temperature range of 500–700 °C with x fixed at 0.06, in which the as-deposited one is given for comparison. Similar to Raman spectra, no crystal grains are detected in either the as-deposited sample or the annealed ones with temperature below 600 °C. Nanocrystallization of a-$Si_{1-x}Ru_x$ thin films is found in XRD spectra when annealing temperature rises to 700 °C. The peaks located at 28.3° and 47.8° are assigned to Si (111) and Si (220) while the peaks located at 25.5°, 32.1°, 41.6° and 46.8° are assigned to Ru_2Si_3 (022), Ru_2Si_3 (400), Ru_2Si_3 (421) and Ru_2Si_3 (241), respectively. Namely, both Si and Ru_2Si_3 nanocrystals are formed in the films treated at 700 °C.

Both the as-deposited and annealed a-$Si_{1-x}Ru_x$ thin films with nominal Ru concentration x fixed at 0.06, are observed by HRTEM. In the as-deposited sample, as shown in Fig. 3(a), small Ru_2Si nanocrystals are observed in the amorphous matrix, which are rarely

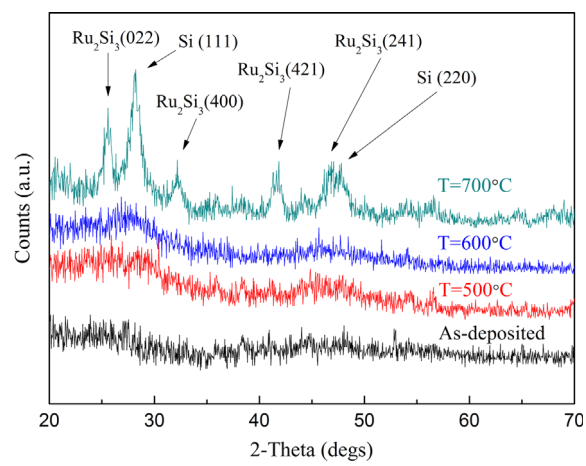

Fig. 2. XRD spectra of a-$Si_{1-x}Ru_x$ thin films with fixed x.

reported in the literature. The inset of Fig. 3(a) shows the diffraction pattern, confirming the co-existence of Ru_2Si nanocrystals with a series of poly-crystal rings and amorphous phase with a halo ring pattern. Possibly due to the low crystalline volume fraction, these nanocrystals are not detected by Raman or XRD. It is commonly considered that the embedded nanocrystals Si grains can localize the photo-creation of dangling bonds near the grain-boundaries hence provide a high stable absorber layer against light soaking [6]. So the ruthenium silicide nanocrystals in a-$Si_{1-x}Ru_x$ thin films are expected to improve the film stability as well. Fig. 3(b) gives the image of annealed sample. The spherical grains should be Ru_2Si_3 nanocrystals coming from a phase transformation of former unstable Ru_2Si [21] and the columnar grains should be Si nanocrystals originating from a MIC process [10]. Two sets of diffraction poly-crystal rings in the inset of Fig. 3(b) refer to Si and Ru_2Si_3, respectively, while the amorphous phase still exists with a halo ring pattern.

Resistivity and TCR of the as-deposited a-$Si_{1-x}Ru_x$ thin films are measured and shown in Fig. 4(a). Significant resistivity reduction has been obtained with the increase of nominal Ru concentration x. This change may be caused by the accept-like state created by substitutional Ru atoms in a-Si network [16]. TCR is an important characterization of material which is sensitive to heat. A negative TCR is obtained in all samples and its absolute value decreases with the increase of x. Due to the high resistance which makes the accurate measurements very difficult, the TCR of intrinsic a-Si thin film is not given here. The low resistivity value and reasonable TCR

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