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Structural, optical and electrical properties of Ti doped amorphous silicon prepared by co-sputtering

Tianwei Zhou, Yuhua Zuo*, Leliang Li, Kai Qiu, Jun Zheng, Qiming Wang

State Key Laboratory on Integrated Optoelectronics, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, PR China

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ABSTRACT

Titanium-doped unhydrogenated amorphous silicon (a-Si: Ti) films were prepared by rf co-sputtering. Structural, optical and electrical properties of a-Si: Ti as a function of Ti content were investigated by RBS(Rutherford Backscattering Spectrometry), XPS(X-ray Photoelectron Spectroscopy), Raman, ESR (Electron Spin Resonance), Spectroscopic Ellipsometry, thermoelectric tests and temperature dependent *I*–*V* tests. Introducing Ti impurity in amorphous Si results in n-type material, room temperature conductivity increases more than three orders of magnitude and activation energy decreases obviously. When Ti content is lower than 2 at.%, the degree of short-range order and defect state density of amorphous Si network improve while the optical bandgap changes little. However, with Ti content higher than 2 at.%, the degree of short-range order decreases and the optical gap of a-Si shrinks. The role of Ti atoms in amorphous Si network is discussed. ESR results confirm that introducing low content of Ti can compensate the dangling bonds of amorphous Si, while with Ti content higher than 2%, most Ti atoms compensate the unpaired electrons in the conduction band tail.

1. Introduction

Intermediate band solar cell (IBSC) is a promising third-generation solar cell to achieve very high efficiency above the S-Q [1] limitation established in 1961. It is based on inserting a half-filled intermediate band in the traditional forbidden band of semiconductor that permits sub-bandgap low energy photons to be absorbed, increasing the current of solar cell while keep the constant output voltage. According to the detailed balance principle, the IBSC has a maximum efficiency of 63.2 at.% [2] for the host material with gap of 1.95 eV. Even though for amorphous Si with bandgap of 1.7 eV, the IBSC efficiency can be over 60% [3].

Doping Ti in crystalline silicon to form impurity band, has been studied as a kind of IBSC material by several groups [4,5]. Other candidate elements are the chalcogen (S,Se,Te) and transition metal Co impurity in silicon, for which an insulator – metal transition has been reported [6–8].However, the theoretical maximum efficiency is limited by the narrow bandgap of crystalline silicon. Since amorphous Si has larger bandgap, is it possible to form intermediate band in a-Si matrix? And what will happen when doping Ti impurity in amorphous Si? Similar articles have been reported about incorporating Ti in GaAs and amorphous Si [9] which has been suggested as a possible IB material candidate and the optical and compositional characteristics of GaAs(Ti) films have been analyzed [10]. Thus it is of interest to understand the fundamental properties with Ti doping in a-Si.

Much work has been done on the doping of transition metals [11], such as Mn, Ni, Fe and Co, in amorphous Si. And there is a detailed review [12] on the properties of amorphous silicon alloys. However, little work has been done on the effect of Ti doping in amorphous Si.

The motivation of the present work is as follows: first, the efficiency of a-Si: PVC is low due to the insufficient utilization of low energy photons; second, hydrogen is usually used to compensate the numerous dangling bonds in amorphous silicon, we expect that titanium has the same effect. Given this, we investigate the structural, optical and electrical properties of titanium-doped amorphous silicon films prepared by co-sputtering in pure argon atmosphere, and discuss the effect of Ti impurity and its concentration on physical properties of the amorphous Si without hydrogen.

2. Material and methods

Titanium-doped amorphous silicon (a-Si: Ti) films were deposited on silicon and quartz substrates respectively, by co-sputtering of Ti and c-Si targets in pure argon atmosphere. Ar gas pressure during sputtering was kept to 3mTorr. The substrate

* Corresponding author.
E-mail address: yhzuo@semi.ac.cn (Y. Zuo).

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temperature and sputtering time were 300 °C and 2 h respectively. The sputtering power of silicon target with diameter of 2 inch was kept to 90 W (4.44 W/cm^2), while the sputtering power of titanium target with diameter of 2 inch varied from 0 to 30 W (1.48 W/cm^2).

The composition of the films was analyzed by Rutherford BackScattering (RBS) spectrometry, and the chemical bonding information was achieved from X-ray Photoemission Spectroscopy (XPS) system with a focused monochromatic Al Kα source for excitation and a concentric hemispherical analyzer at constant pass energy (100 eV). Raman scattering measurements were applied to characterize the structure of the films. The excited source is 488 nm Ar^+ laser and the power is kept to below 2 mW with focusing diameter of about 10 μm (power density is below 25 μW/μm^2). The absorption property was studied by J.A.Woollam M-2000 DI Spectroscopic Ellipsometry (SE) in the spectrum range of 200–1700 nm, deducing from $\alpha = 4\pi k/\lambda$. And the thicknesses of the samples were about 514–525 nm, deduced from SE data. The Seebeck coefficient was measured by a four-probe method using a thermal transport option in Quantum Design physical property measurement systems (PPMS) at high vacuum (10^{-5} Pa). A resistive heater was connected to one end of the film, while the other end was mounted on a cold sink. The dark conductivity was measured for samples having planar geometry with Al electrodes under vacuum to reduce the surface contamination. The thermal activation energy of the dark conductivity was studied for different Ti contents, for the temperature range from 300 K to 360 K. The ESR was performed at 77 K with a JES-FA200 ESR Spectrometer operating at X-band with 100 kHz modulation. The values of samples were determined by using Mn^{2+} and DPPH as the standard materials.

3. Results

3.1. 1Titanium content

The inset of Fig. 1 shows RBS spectra of a-Si: Ti film with Ti sputtering power of 10 W. It indicates a homogeneous and constant distribution of Ti along the growth direction of the film. A concentration of titanium atoms of 1.5 × 10^{21} cm^{-3} (3 at.%) is determined from the area of titanium incorporation in a-Si film. It is shown from Fig. 1 that Ti content increases with Ti target sputtering power and the Ti content can be up to at 9%.

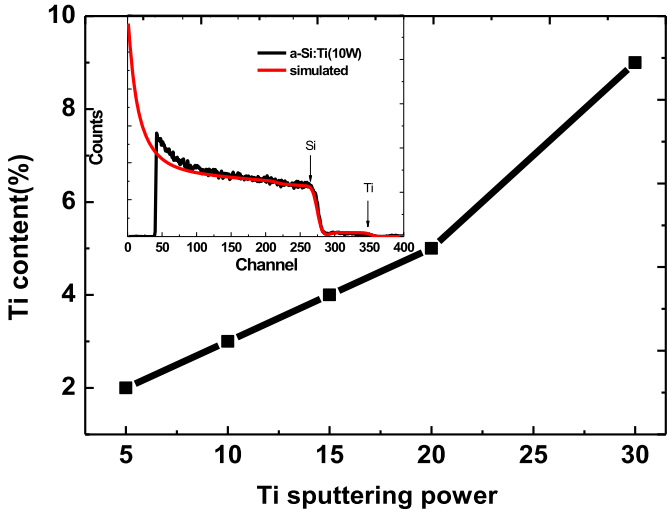

Fig. 1. Ti content as a function of Ti target sputtering power (Inset is the RBS spectra of a-Si: Ti film with Ti target power of 10 W).

3.2. Composition and structure analysis

3.2.1. XPS analysis

XPS is a sensitive surface analysis technique, which is capable of providing information about elements and chemical bonding of the surface.

XPS spectra of silicon and titanium 2p lines from co-sputtered samples with titanium content of 0% and 9 at.% are shown in Fig. 2.

An obvious chemical shift between two samples can be observed in Fig. 2(a). The peak positions of 2p line are at 99.46 eV for pure Si and at 98.77 eV for the sample with titanium content of 9%, respectively. The shift of 0.69 eV compared to elemental Si indicates the existence of titanium silicide in the a-Si: Ti film. That means Ti atoms do enter in the amorphous Si network and form Si–Ti bonding at the surface of a-Si: Ti films. In addition, the asymmetric peaks for both 99.46 eV and 98.77 eV can be decomposed to the $2p_{1/2}$ and $2p_{3/2}$ signals, not shown in Fig. 2(a).

The XPS spectra of the Ti 2p peaks in Fig. 2(b) indicates that Ti can be existed in two forms, either Ti oxide or Ti silicide. The peak at 465.0 eV is corresponding to the bonding energy (BE) of Ti $2p_{1/2}$ oxide peak which is easily distinguished, since oxide has a large chemical shift compared to metal states [13]. As the samples were

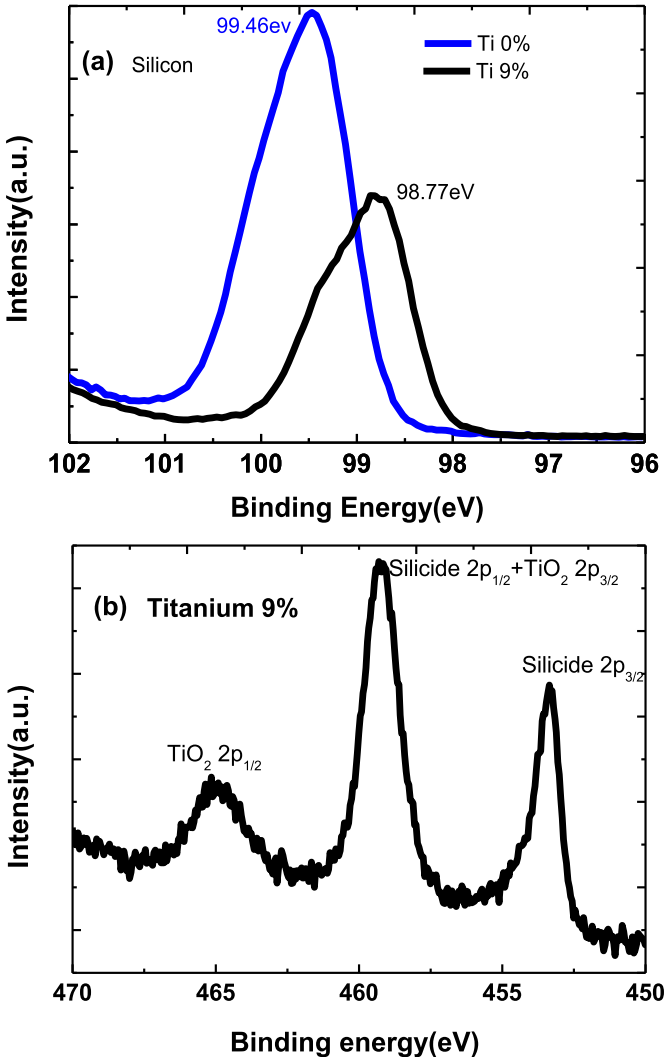

Fig. 2. XPS spectra of (a) Si and (b) Ti in samples with titanium content of 0 at.% and 9 at.%.