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Band engineering of amorphous silicon ruthenium thin film and its near-infrared absorption enhancement combined with nano-holes pattern on back surface of silicon substrate

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ABSTRACT

Silicon is widely used in semiconductor industry but has poor performance in near-infrared photoelectronic devices because of its bandgap limit. In this study, a narrow bandgap silicon rich semiconductor is achieved by introducing ruthenium (Ru) into amorphous silicon (a-Si) to form amorphous silicon ruthenium (a-$Si_{1-x}Ru_x$) thin films through co-sputtering. The increase of Ru concentration leads to an enhancement of light absorption and a narrower bandgap. Meanwhile, a specific light trapping technique is employed to realize high absorption of a-$Si_{1-x}Ru_x$ thin film in a finite thickness to avoid unnecessary carrier recombination. A double-layer absorber comprising of a-$Si_{1-x}Ru_x$ thin film and silicon random nano-holes layer is formed on the back surface of silicon substrates, and significantly improves near-infrared absorption while the leaky light intensity is less than 5%. This novel absorber, combining narrow bandgap thin film with light trapping structure, may have a potential application in near-infrared photoelectronic devices.

1. Introduction

As one of the most important material in semiconductor industry, silicon has been widely used in photoelectronic devices such as solar cells and detectors. However, silicon based photoelectronic devices have poor performance in near-infrared region owing to the bandgap limit, which means that incident photons with energy below 1.12 eV cannot be absorbed. Thus, narrow bandgap components are in demand for device to harvest near-infrared light. Band engineering is one of the effective ways to achieve narrow bandgap semiconductors and promote the conversion efficiency of photoelectronic devices. For instance, SiGe alloy is a common material which is usually served as bottom absorber layer in Si-based multijunction thin film solar cells to expand the responding of devices to a long wavelength, making a better utilization of solar spectrum [1,2]. By varying Ge fraction, the bandgap of SiGe thin film can be adjusted to 0.78 eV in a very high Ge fraction ($Si_{0.048}Ge_{0.952}$) [3]. Besides, band engineering with other elements are also studied to optimize the responding spectrum of Si-based thin film solar cells. For example, rare earth elements are utilized to achieve better exploitation of the solar spectrum with the abilities of down-conversion or up-conversion [4–6]. It is reported that ruthenium (Ru) silicide may have promising properties in band engineering as well. Filonov et al. [7] demonstrate Ru_2Si_3 to be a direct bandgap semiconductor with energy gap of 0.41 eV by *ab initio* calculations while Lenssen et al. [8] find it a bandgap of 0.84 eV by experiments. This wide range energy bandgap shift of ruthenium silicide indicates that a possible Si-rich narrow bandgap absorber layer might be achieved by a-$Si_{1-x}Ru_x$ thin film.

It is well known that amorphous materials contain defects which would increase the recombination of charge carries and lower the performance of photoelectronic devices. A very simple way to lower the recombination probability is to reduce the thickness of amorphous thin film used in the device while the reduced thickness is sustainable for high efficient light harvest. Therefore, specific light trapping technique is crucial for such high efficient absorber with a finite thickness. Vynck et al. [9] demonstrated a thin dielectric membrane containing a random pattern of circular holes going through the entire film thickness, named as two-dimensional disorder media, is effective for broadband light absorption. In our formulation, depositing thin film on silicon nanostructured surface would naturally form a layer containing the same pattern of the underlying nanostructures. And these nanostructures can be prepared through several approaches including femtosecond laser

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irradiation [10], chemical etching [11] and reactive ion etching [12]. Similar system on the front surface has been fabricated for anti-reflection, comprising of amorphous silicon (a-Si) nanograss layer on top of silicon nanofrustums [13]. Considered the a-$Si_{1-x}Ru_x$ thin film is a narrow bandgap layer which usually serves as bottom absorber in multi-layer photoelectronic device, the nanostructures used to create random pattern for the covering thin film should be constructed on the back surface of silicon substrates. These nanostructures designed on the back surface are also effective for light trapping [14].

Based on above considerations, we introduce Ru instead of Ge, into a-Si to adjust the bandgap of a-$Si_{1-x}Ru_x$ thin films. Since the structural and electrical properties of a-$Si_{1-x}Ru_x$ thin films have been reported in our early researches [15,16], in this work, efforts are focused on optical properties of the thin films. Random nano-holes are fabricated on the back surface of silicon substrates by chemical etching, and a layer of a-$Si_{1-x}Ru_x$ thin film is deposited on them subsequently. To balance the absorption and carrier recombination of a-$Si_{1-x}Ru_x$ thin films, the thickness is set to 100 nm which is comparable to the diffusion length of the minority charge carriers in a-Si [17]. The layer of silicon nano-holes and the layer of covering thin film could form a double-layer absorber on the back surface of silicon substrates. It is found that the bandgap decreases dramatically to 0.86 eV with only 1% Ru and reaches about 0.51 eV at a Ru concentration of 8%, and the double-layer absorber on the back surface significantly enhances the near-infrared light absorption while the leaky light intensity is less than 5%.

2. Experimental details

The random nano-holes pattern on the back surface of silicon substrates was prepared by Ag-catalyzed chemical etching. Firstly, silicon substrates of high purity (~3000 Ω·cm) were immersed into the silver-ammonia solution ($AgNO_3$/NaOH/$NH_3{\cdot}H_2O$/$C_6H_{12}O_6$ = 20:24:11:30 vol ratio; concentrations are 2%, 2%, 2% and 1.5%, respectively) to disperse Ag nanoparticles onto the back surface. Then these substrates were etched in etchant acid solution (HF/H_2O_2 = 2:5 vol ratio; concentrations are 10% and 0.6%, respectively). And finally Ag nanoparticles were removed after etching by immersing into mixed acid (H_2SO_4/HF = 3:1 vol ratio; concentrations are 98% and 40%, respectively) and HNO_3 (10%), successively.

100 nm thick a-$Si_{1-x}Ru_x$ thin films were deposited on the silicon substrates containing random nano-holes prepared in the last step and also on quartz substrates by RF magnetron co-sputtering. The chamber was pumped to a base pressure of 5×10^{-4} Pa and the substrates were heated to 300 °C before deposition. The RF power was set to 200 W with a power density of about 2.55 W cm^{-2}. Argon (Ar) flow served as working gas was kept at 90 sccm (standard cubic centimeter per minute) and chamber pressure was 0.5 Pa. To introduce Ru atoms, several pure Ru (99.95%) chips were fixed on a 4 in. high purity Si target (99.999%). The Ru nominal concentration, varying from 0.3% to 8%, was estimated by the target coverage proportion of Ru chips and the sputtering yields were taken into account. Annealing treatment was carried out in a quartz tube in Ar atmosphere at 700 °C for 30 min.

The optical properties of the thin films deposited on quartz substrates were carried out by spectroscopic ellipsometry (SE) method with SENTECH SE850 ellipsometer. Ellipsometric parameters (Ψ, Δ) were collected at an incident angle of 50° and a range of 280–2500 nm. An optical stack of air/a-$Si_{1-x}Ru_x$/quartz was created for modeling and Tauc-Lorentz model was employed to the a-$Si_{1-x}Ru_x$ layer. From well fitted data of all samples, optical properties and optical bandgap were deduced. X-ray diffraction spectra (XRD) were measured by PANalytical X'pert HighScore XRD instrument. The surface morphology was characterized by field emission scanning electronic microscopy (SEM, Hitachi S-4800). The absorption of the back side double-layer absorber was measured at normal incidence by a Vis-NIR spectrophotometer equipped with an integrating sphere detector in a range of 400–1700 nm.

3. Results and discussion

The SE method is a common way to measure optical properties of thin films through the change in polarized light upon light reflection on samples. Optical constants, band structure and other properties can be deduced by a well constructed optical model using the ellipsometric parameters (Ψ, Δ) collected from samples. Here, an optical stack of air/a-$Si_{1-x}Ru_x$/quartz is constructed and Tauc-Lorentz (T-L) model which is commonly employed to fit a-Si thin films [18] are applied for a-$Si_{1-x}Ru_x$ layer. The T-L model is expressed as following equation:

$$\varepsilon_2(E) = \begin{cases} \dfrac{AE_0C\left(E-E_g\right)^2}{\left(E^2-E_0^2\right)^2+C^2E^2}\dfrac{1}{E} & (E > E_g) \\ 0 & (E \le E_g) \end{cases} \quad (1)$$

where ε_2, A, E_0, C and E_g represent the imaginary part of dielectric function, the oscillator strength, the oscillator resonance energy, the oscillator broadening parameter and the Tauc optical bandgap, respectively. The real part of dielectric function ε_1, is derived by the well-known Kramers-Kronig relations [18]. Then the extinction coefficient k could be described in terms of the values of ε_1 and ε_2:

$$k = \sqrt{\frac{1}{2}\left[\left(\varepsilon_1^2+\varepsilon_2^2\right)^{1/2}-\varepsilon_1\right]} \quad (2)$$

Fig. 1a shows the calculated k versus wavelength. The k of intrinsic a-Si thin film decreases drastically in visible range and drops to zero in near-infrared range. With added Ru atoms, the slope of k curve becomes smaller and the value of k is still notable in near infrared range. Furthermore, the absorption coefficient α is calculated with k curve by:

$$\alpha = 4\pi k/\lambda \quad (3)$$

As shown in Fig. 1b, a significant enhancement of absorption coefficient α is achieved with added Ru atoms, especially in near-infrared range. The absorption coefficient of intrinsic a-Si decreases dramatically at wavelength longer than 750 nm, making it unable to collect near-infrared photons. However, with only 0.3% Ru, the absorption edge of a-$Si_{1-x}Ru_x$ moves from 798 nm to 1231 nm. Moreover, the value of absorption coefficient remains above 10^4 cm^{-1} even at 2000 nm for sample with maximum Ru concentration x = 0.08. It is worth to point out that the absorption coefficient of Si rich a-$Si_{1-x}Ru_x$ is much higher than that of Ge rich SiGe alloy [19] (88% Ge, also plotted in Fig. 1b for comparison) in infrared range. Obviously, adding of Ru atoms greatly improves the low energy photon collection ability of a-$Si_{1-x}Ru_x$ thin films. A higher absorption coefficient is of significance to achieve high efficient absorber with only 100 nm thickness.

According to Tauc law [20], a typical relation describing light absorption in amorphous semiconductor, the optical bandgaps of a-$Si_{1-x}Ru_x$ thin films are calculated and depicted in Fig. 2. The Tauc law can be written as:

$$\sqrt{(ah\upsilon)} = B\left(h\upsilon - E_g\right) \quad (4)$$

where B is a constant related to material, $h\upsilon$ is the incoming photon energy and E_g is the optical bandgap. As shown in Fig. 2, E_g is plotted by extending each linear fit to X-axis. The slope of linear line denotes constant B and the intercept is equal to E_g. Result of E_g is depicted in the inset of Fig. 2. The values decrease rapidly