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Journal of Non-Crystalline Solids



Reversible changes in temperature dependence of electric conductivity of hydrogenated amorphous silicon caused by proton irradiation



JOURNAL OF NON-CRYSTALLINE SOLIDS

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ARTICLE INFO

Article history: Received 30 January 2014 Received in revised form 18 March 2014 Accepted 24 March 2014 Available online 15 April 2014

Keywords: Amorphous semiconductors; Hydrogenated amorphous silicon; Radiation defects; Electric conduction mechanism; Temperature dependence

ABSTRACT

We investigate temperature dependence of electric conductivity and photoconductivity of hydrogenated amorphous silicon (a-Si:H) thin films due to energetic proton irradiation and clarify the change in dominant electric conduction mechanism. We also investigate variations of the temperature dependence after proton irradiation at different temperatures and the recovery from radiation damage due to thermal annealing. The results show that the high fluence proton irradiation changes the dominant electric conduction mechanism from the band transport of thermally excited carriers through the extended states to the hopping transport based on the carrier transport via localized states near the Fermi level. The hopping conduction has the weak temperature dependence which disappears at elevated temperature and the strong temperature dependence based on the band conduction appears again. Also, the proton irradiation at high temperature never provoke the hopping conduction. However, the band conduction after irradiation is not completely restored even after thermal annealing, indicating that thermally stable radiation defects remain. We conclude that these dominant electric conduction mechanism changes originated from proton irradiation and thermal annealing, and are simply caused by the increase or decrease in localized density of states.

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1. Introduction

Since progress in high energy physics and space technologies requires development of semiconductor devices with high radiation resistance, radiation effects on semiconductor devices and materials have been investigated for decades [1,2]. In order to improve radiation resistance of semiconductor devices, it is necessary to understand variation of semiconductor properties due to radiation exposure, e.g. electric conductivity (dark conductivity: DC), photoconductivity (PC), carrier concentration, and carrier type. Radiation effects on crystalline silicon (c-Si), which is a principal semiconductor material, have been extensively investigated and are substantially understood [3] whereas radiation effects on amorphous semiconductors are less well investigated and poorly understood.

Hydrogenated amorphous silicon (a-Si:H) is used as a material for photoelectric devices such as photo sensors and solar cells, and is also expected to be utilized in severe radiation environments such as space, accelerator and nuclear facilities because it has been reported that a-Si: H devices have higher radiation resistance than c-Si devices [4,5]. The radiation effects on a-Si:H have been investigated on the basis of the comparison of the light-induced degradation (Staebler–Wronski effect [6]) and the radiation effects on c-Si [7–13]. However, some researchers have reported unique phenomenon like the (temporal) increase in DC and PC [7,14–17] and the anomalous enhancement of radiation induced conductivity [18,19], and they could not be explained by the general interpretation of radiation effects on semiconductor materials. Therefore, the radiation effects on a-Si:H have not yet been systematically understood. This may be because the radiation effects on a-Si:H is usually unstable and is immediately restored with time even at room temperature, and thus, it is difficult to obtain the systematic knowledge.

It is very important not only to investigate radiation effects on a-Si:H on the basis of the comparison to the SW effect, but also to investigate on the basis of the comparison to that on hydrogen-free amorphous silicon (a-Si). Hydrogen-free a-Si has a very high dangling bond density (above 10^{20} cm⁻³) and the electric conduction is mainly dominated by the hopping transport of carriers via localized states. However, hydrogenation results in the drastic decrease in dangling bond density $(10^{15}-10^{16} \text{ cm}^{-3})$, since hydrogen atoms terminate the dangling bonds in a-Si. The decrease in dangling bond density provides the decrease in hopping transport and the increase in band transport of thermally excited carriers through the extended states. Consequently, hydrogen atom is an essential element for a-Si:H semiconductors and the hydrogen concentration strongly affects the electrical properties. However, the relationship between the decrease in dangling bond density due to hydrogenation and the increase in defects density due to irradiation remains to be elucidated. At least, it has been shown that ion irradiation does not induce the decrease in hydrogen concentration in a-Si:H [20].

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Recently we have investigated radiation effects on a-Si:H thin films and have clarified complicated variations of DC and PC due to energetic charged particles [15,16,18,20,21]. Heavy ion irradiation induces the decrease in DC and PC at first, and the increase in DC and the loss of photoconduction appear in the high fluence regime. On the other hand, high energy proton and electron irradiations induce the increase in DC and PC at first, and the decrease in DC and PC appears in the high fluence regime. Interestingly, these combined variations are observed in the case of middle energy protons like 100 keV. Although it is generally known that both DC and PC of semiconductor materials decrease with increasing fluence because of the generation of radiation defects (deep level defects), the complicated DC and PC variations in a-Si:H could not be explained by such a simple interpretation. One of the effective methods for clarifying the radiation effects is to investigate the temperature dependence of DC and PC. The temperature dependence reflects the electric conduction mechanism, and therefore the variation of temperature dependence due to irradiation may indicate the change in dominant electronic conduction. As mentioned above, however, recovery from the radiation defects begins immediately after irradiation and it is difficult to distinguish the variations due to thermal annealing and the original temperature dependence. Because of this, the research on temperature dependence of electric conductivity after irradiation has never been reported. In order to overcome this difficulty, we developed an in-situ temperature-variable current-voltage (I-V)measurement system, which made it possible to investigate the unstable nature of radiation effects. A stable light source was installed in this system to measure PC as well as DC.

In this paper, we report the change in temperature dependence of DC and PC immediately after proton irradiation. The variations of temperature dependence due to proton irradiation at different temperatures and the thermal annealing after irradiation are investigated.

2. Experimental

2.1. Sample preparation

The samples used in this study were device-grade undoped a-Si:H thin films fabricated on glass substrates by Plasma Enhanced Chemical Vapor Deposition (PECVD). The excitation frequency, the substrate temperature during deposition, and the gas flow rate were 13.56 MHz, 453 K, and SiH₄/H₂ = 20/100 sccm, respectively. The size of the active area was $8.0 \times 8.0 \text{ mm}^2$ and interdigitated aluminum ohmic electrodes were formed on the sample [21]. Typical characteristics of the samples are listed in Table 1. The film thickness was measured by a surface profiler. The mass density and the hydrogen concentration were determined experimentally by using Rutherford Backscattering Spectroscopy (RBS) and Elastic Recoil Detection Analysis (ERDA).

2.2. Proton irradiation

The samples were irradiated with 100 keV protons at various temperatures at the Takasaki Ion Accelerators of advanced Radiation Application (TIARA), Japan Atomic Energy Agency (JAEA) [22]. A raster beam scanning system was used for uniform irradiation of the whole

Table 1
Typical characteristics of the samples and the values of DC and PC

Film thickness	0.30 µm
Density	2.30 g/cm ³
Hydrogen concentration	11.6 at.%
DC (annealed)	1.5×10^{-10} S/cm
DC (light-soaked)	5.3×10^{-11} S/cm
PC (annealed)	$9.1 imes 10^{-5}$ S/cm
PC (light-soaked)	1.2×10^{-5} S/cm

area of the sample. The fluctuation of beam uniformity was estimated to be within \pm 5%. The fluctuation of proton irradiation fluence was estimated to be \pm 10%, which was determined by the beam current, the irradiation time, and the irradiation area. The projected ranges of 100 keV protons are larger than the thickness of the a-Si:H film and deposit their energy almost uniformly through the a-Si:H film, according to the Monte Carlo simulation code, TRIM [23]. Thus, no passivation by the implanted hydrogen atoms of dangling bonds in the a-Si:H films is expected. In the TRIM calculation, default values of displacement energy installed in the program were used: 15 eV for Si and 10 eV for H. Electronic energy deposition (*S*_e), nuclear energy deposition (*S*_n), *S*_n/*S*_e, fluence per unit dpa (displacement per atom, ϕ_{dpa}), and projected range (*R*) of ions in the undoped a-Si:H were 1.1×10^2 eV/nm, 0.16 eV/nm, 1.5×10^{-3} , $4.5 \times 10^{18} \text{ cm}^{-2}$, and 0.89 µm, respectively. Values of *S*_e, *S*_n, and ϕ_{dpa} are average values along the depth direction.

2.3. Temperature dependence of electric conductivity

The current-voltage (I-V) characteristics of the samples and its temperature dependence were measured in-situ in an irradiation chamber under dark conditions for DC and under light illumination for PC. The light spectrum and intensity were AM-0 (Air Mass zero) and 136.7 mW/cm² (1 sun), respectively. The fluctuation of light intensity was estimated to be within $\pm 0.5\%$. Hereinafter, DC is defined as the conductivity measured under dark conditions and PC is defined as the difference between the DC and the conductivity under light illumination. The voltage sweep range was between -40.0 V (-2.00 kV/cm)and +40.0 V (+2.00 kV/cm) and the electric conductivity was derived from the slope of *I–V* characteristics. The typical values of DC and PC are listed in Table 1. The temperature during measurements was 298 K. The values under both "annealed" and "light-soaked" conditions are shown in the table. It is well known that the decrease in DC and PC is induced by long time light illumination (the Staebler–Wronski effect) [6]. The "annealed" values in Table 1 were measured when the sample was thermally annealed and the light-induced degradation was completely eliminated. Also, the "light-soaked" values were the stabilized values when the light-induced degradation was sufficiently induced by the long time light illumination.

Fig. 1 shows variations of DC and PC of the undoped a-Si:H as a function of 100 keV proton fluence at room temperature, which was reported by us in a previous work [20]. The sample was light-soaked before proton irradiation. The fluctuations of DC and PC values were estimated to be within $\pm 3\%$ and $\pm 4\%$ respectively, which were mainly



Fig. 1. DC and PC variations of the undoped a-Si:H as a function of 100 keV proton fluence [20].

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