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Effect of illumination on hydrogenated amorphous silicon thin films doped with chalcogens

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ABSTRACT

Hydrogenated amorphous silicon thin films doped with chalcogens (Se or S) were prepared by the decomposition of silane (SiH_4) and H_2Se/H_2S gas mixtures in an RF plasma glow discharge on 7059 corning glass at a substrate temperature 230 °C. The illumination measurements were performed on these samples as a function of doping concentration, temperature and optical density. The activation energy varied with doping concentration and is higher in Se-doped than S-doped a-Si:H thin films due to a low defect density. From intensity versus photoconductivity data, it is observed that the addition of Se and S changes the recombination mechanism from monomolecular at low doping concentration films to bimolecular at higher doping levels. The photosensitivity (σ_{ph}/σ_d) of a-Si, Se:H thin films decreases as the gas ratio H_2Se/SiH_4 increased from 10^{-4} to 10^{-1}, while the photosensitivity of a-Si, S:H thin films increases as the gas ratio H_2S/SiH_4 increased from 6.8×10^{-7} to 1.0×10^{-4}.

1. Introduction

Hydrogenated amorphous silicon (a-Si:H) thin films have been studied during the last three decades with growing interest because of their potential applications in electronic and optoelectronic devices. Current interests in hydrogenated amorphous silicon thin films and its alloys as promising candidates for the realization of advanced sensing system such as gas sensors [1,2], pixel detector for high energy particles [3,4], optical imaging [5], active matrix displays [6,7] and solar cells [8–10] is clearly seen from these publications. Hydrogenated amorphous silicon thin films have high optical absorption, low temperature deposition (<300 °C) is possible, high uniformity over large area, few constraints on substrate size, material, or topology.

Most of the studies were made on preparation and investigation of the properties of a-Si:H alloy with tetrahedrally co-ordinated elements such as C and Ge [11]. The effect of alloying halogen such as F or Cl [12] to a-Si:H was also investigated and has shown to have potential in certain applications [13]. So far a-Si, C:H has emerged as leading contender in large bandgap alloys in amorphous silicon based photovoltaic devices by serving as photon energy absorbing window layers in multi-junction cells [9]. Despite this success, fundamental problems of the efficiency and the long-term stability of the material have not been solved due to the photoinduced degradation in a-Si:H thin films, which is associated with light-induced metastable Si dangling-bond defect [14,15]. This effect hampers the utilization of amorphous silicon and its alloy in solar cells on a large scale and since then, intensive research has been carried out to elucidate the degradation mechanism [16–18] and to improve the stability.

Recently the selection of Se and S as the doping element, as grown by capacitively coupled RF glow discharge decomposition of silane (SiH_4) and hydrogen sulfide (H_2S) and hydrogen selenide (H_2Se) diluted in helium (He), terminate the silicon dangling bonds in the same way as hydrogen as shown in Fig. 1 [15]. The temperature dependant conduction mechanism of Se and S-doped a-Si:H thin films have been studied by Sharma et al. [19]. Two types of conduction mechanism were observed. The conduction was found

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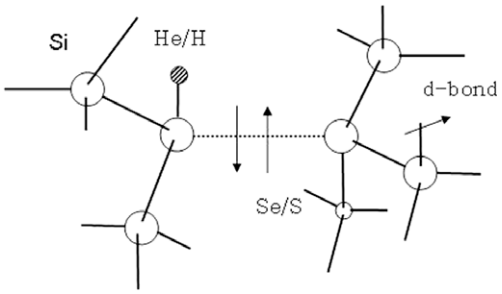

Fig. 1. Schematic illustration for dangling bond and doping atom.

to be of activated type in the high temperature range while in the low temperature range (less than 370 K), it was observed to follow variable range hopping.

Photoconductivity (PC) plays a central role in the study of hydrogenated amorphous silicon (a-Si:H). It is associated not only with carrier excitation, trapping and radiative and non-radiative recombination, but is also associated with various transport mechanisms of extended state conduction and hopping through the distribution of localized band tail states. The presence of metastable defects in a-Si:H was discovered by Beyer, Fritzsche et al. [20,21] from photoconductivity measurements. It was shown that photoinduced metastable defects are created within the material upon recombination of excess carriers. This photoinduced degradation, which is known as the Staebler–Wronski Effect (SWE), is reversible and the initial properties can be recovered by annealing the films at a temperature of 200 °C in dark [19]. It is an intrinsic effect and observed in the device quality of amorphous silicon alloys. It is not associated with impurities and can be considerably reduced by pursuing preparation conditions which promote a dense, void free structure with quasi-crystalline regions and low hydrogen concentration such that recombination takes place without structural changes [3]. Light incident on a-Si:H causes metastable Si dangling bond (DB) defects to form with the result of increased carrier trapping and decreased photoconductivity. Much theoretical and experimental effort has been put into understanding the SWE, but a comprehensive explanation has yet to be achieved [22].

A light induced increase in the dark conductivity frequently referred to as persistence photoconductivity (PPC), has been observed for a-Si:H thin films fabricated under wide range of deposition conditions and also for compensated a-Si:H films and doping modulated amorphous silicon multilayer [23–26] and more recently in S-doped a-Si:H films [27]. It seems that the study of the influence of additional instabilities introduced by impurities such as Si–Se of interest as a test of the feasibility of neutralizing rather than eliminating the SWE. The electrical transport in hydrogenated amorphous silicon (a-Si:H) is sensitive to doping concentration. Doping can also have an effect on the temperature dependence of dc dark and photoconductivity.

The aim of this work is to understand the influence of chalcogens as dopants in hydrogenated amorphous silicon thin films on their photoconductivity. Tests were performed on a-Si, Se:H and a-Si, S:H thin films as a function of temperature, doping concentration and optical density in a specially designed vacuum cryostat in the temperature range 27–200 °C. The light was illuminated on all the films with IR filter under the illumination of white light at 100 m watt/cm^2. The results of intensity dependence of photoconductivity of a-Si, Se:H and a-Si, S:H thin films were also measured at room temperature. An estimate of the photosensitivity of the two materials has also been made.

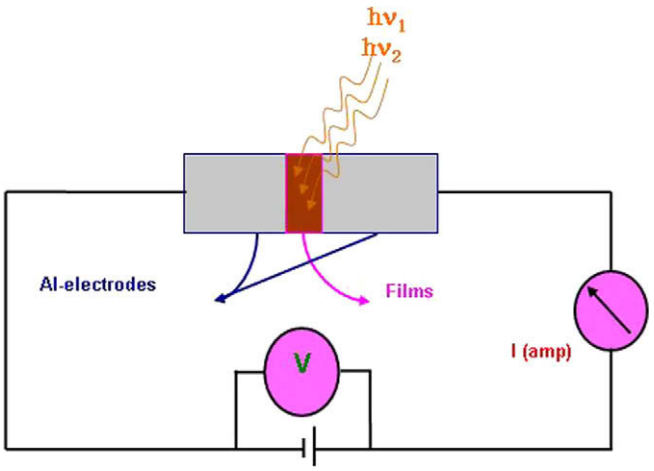

Fig. 2. Schematic diagram for dark and photo conductivity measurements of Se and S-doped a-Si:H thin films.

2. Experimental

Dark and photoconductivity measurements have been performed on a-Si, Se:H and a-Si, S:H thin films prepared by plasma enhanced chemical vapor deposition (PECVD). The schematic diagram for photoconductivity measurements of thin films is shown in Fig. 2. The H_2Se and H_2S vapor were mixed with silane gas (SiH_4) in order to achieve Se and S doping, respectively [28]. Thickness of the films was measured using Surface Profiler (DekTaK3). The absence of sharp peaks in X-ray diffraction (XRD) pattern confirmed the amorphous nature of the films. For conductivity measurements, the aluminum contacts in a coplanar configuration were evaporated. Initially the films annealed at 200 °C in a specially designed vacuum cryostat, to remove surface adsorption and metastable defects in the Se and S-doped a-Si:H thin films. The measurements were then carried out under a vacuum higher than 10^{-3} torr. The dark conductivity was measured once again upon warming. The photoconductivity was measured by illuminating the white light of a tungsten halogen lamp of intensity of 100 m watt/cm^2 that was calibrated using a standard detector (Hamamatsu S. 2281, Photodiode), under vacuum in temperature range of 27–200 °C. Intensity dependant of photoconductivity and persistent photoconductivity were also measured at room temperature using the series of optical density filters.

3. Theory

3.1. Photoconductivity phenomenon

Photoconductivity is the increase in electrical conductivity of a photosensitive material when it is exposed to electromagnetic radiation. It occurs when carriers are optically excited from non-conducting to conducting states. Steady state photoconductivity involves three mechanisms [29]:

1. Absorption of photons by the material and generation of free electron–hole pairs.
2. Separation of electrons and holes and transport of the mobile photo-generated carriers.
3. Recombination of excess free electrons and holes via recombination centers which are located between the quasi Fermi levels for electrons and holes respectively.

Under the action of absorbed light, the densities of charge carriers electrons (n) and holes (p) increase compared with their values at thermal equilibrium. If n_0 and p_0 denote the equilibrium densities