

The nature of mobile hydrogen in a-Si:H—Electrochemical studies

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Abstract

Electrochemical studies of both the a-Si:H based metal/oxide/semiconductor structures and a-Si:H modified Pt electrode as a part of two-electrode cell compartment with electrolyte were performed to obtain information on the nature of mobile hydrogen in a-Si:H. We assume, that the complex formed by a hydrogen molecule and a silicon dangling bond (the origin of D_h states) provides for mobile hydrogen. Information on the process of electron selfexchange (hopping) in a-Si:H driven by diffusion in the presence of a concentration gradient of redox centers is obtained. The capability of the electrochemical methods for studying the role of hydrogen in degradation of a-Si:H caused by bias annealing and/or illumination is demonstrated. Also, it was shown that because of the unique electrocatalytic features of the a-Si:H modified Pt electrode, the latter can act as a “programmable” and selective sensor of heavy metal ions and/or metal complexes.
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Keywords: a-Si:H; Hydrogen diffusion; Gap states; Dangling bond; Semiconducting electrode; Redox centers

1. Introduction

Hydrogenated amorphous silicon (a-Si:H) is widely used in optoelectronic device applications due to both the advantages and low cost of the large area technology and favorable optical properties of a-Si:H. Especially a-Si:H based solar cells should be mentioned as one of leading photovoltaic devices

converting sunlight directly into electricity. This material absorbs solar radiation 40 times more efficiently than does the crystalline silicon. Unfortunately, a-Si:H based solar cells suffer from the well-known light-induced degradation, the so-called Staebler–Wronski effect (SWE) which has been an outstanding subject since its discovery (Staebler and Wronski, 1977). The elucidation of SWE and its microscopic origin has attracted intense scientific studies. Very early it has been noted that the SWE involves creation of metastable silicon dangling bond (DB) defects at densities of 5×10^{15} – $5 \times 10^{17} \text{ cm}^{-3}$ as measured by electron spin resonance

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Nomenclature

a-Si:H	hydrogenated amorphous silicon	Q-DLTS	charge deep-level transient spectroscopy
CVAM	cyclic voltammetry	RT	room temperature
DB	dangling bond	SSVAM	steady-state voltammetry
ESR	electron spin resonance	SWE	Staebler–Wronski effect
MOS	metal/oxide/semiconductor		

(ESR) technique (Street, 1991) with the result of enhanced charge carrier trapping and reduced photoconductivity. Annealing of a-Si:H samples at temperatures above 180 °C restores the state before light illumination. In spite of much theoretical and experimental effort put into the understanding of the SWE, many unresolved issues still remain. The most serious ones are the exact role of hydrogen, its local bonding configurations, origin of the mobile hydrogen, and presence of more than one metastable defect. Recently, a comprehensive model has been suggested (Nádaždy and Zeman, 2004), which incorporates the latest knowledge about the SWE and resolves inconsistencies in previous manifold concepts. It should be noted that the same metastable silicon DB defects are created whenever charge carriers are injected into a-Si:H (Wehrspohn et al., 2003). The latter limit the performance of a-Si:H based thin film transistors. Both above mentioned effects have a common cause, and it is of considerable importance to understand it at a microscopic level. Only the understanding at the microscopic level will ameliorate the deleterious influence the SWE has.

It was demonstrated that the charge deep-level transient spectroscopy (Q-DLTS) technique is a powerful method for observation of gap states in a-Si:H (Nádaždy et al., 1997). The Q-DLTS spectra of undoped a-Si:H change as a function of the Fermi level position in accordance with the improved defect-pool model (Powell and Deane, 1996). Influence of both the bias annealing and illumination on the distribution of gap states in a-Si:H thin films of sandwiched structures was proved (Nádaždy et al., 1997, 2000). The biasing of a-Si:H to negative potential with respect to the reference electrode gives rise to the excess of positively charged D_h states above midgap (low-temperature part of Q-DLTS signal). In the case of the positive biasing these states are suppressed and negatively charged D_e states below midgap dominate (high temperature part of Q-DLTS signal).

Hydrogen is known to play a dominant role in the stabilization and annealing properties of the metastable DB defects (Street, 1991). Previous experimental and theoretical results indicate that the SWE is intimately related to short and/or long range hydrogen diffusions. Therefore, a more detailed understanding of hydrogen diffusion in undoped a-Si:H is a pre-requisite for the explanation of light- and charge-carrier injection-induced metastability. In a-Si:H hydrogen exists in different forms such as SiH, SiH₂, H₂, clusters of SiH. Recent NMR and spin echo double resonance experiments (Fedders et al., 2000) provide convincing evidence that in high-quality a-Si:H nearly 40% of the incorporated hydrogen is in the form of hydrogen molecules. These hydrogen molecules are individually trapped in an amorphous equivalent to a tetrahedral T_d site. Ab initio pseudopotential calculations of hydrogen interaction with a-Si showed (Van den Walle and Tuttle, 1999) that the existence of an over-coordinated complex created with two hydrogen atoms placed in the DB region was possible. This complex introduces a deep energy level in the upper part of the band gap. The additional calculations (Van den Walle and Tuttle, 1999) indicate that also a configuration, in which a hydrogen molecule is placed near a DB, is close in energy to the complex with two hydrogen atoms. On the basis of these facts we have proposed (Zeman et al., 2003) a microscopic configuration, in which a positively ionized hydrogen molecule forms a hybrid bond with a DB that introduces energy levels into the upper part of the band gap. These energy levels correspond to the positively charged D_h states, revealed as a low-temperature Q-DLTS signal (Nádaždy et al., 1997). The above-mentioned microscopic configuration provides for the mobile hydrogen created via the annihilation of D_h states in the early stage of light soaking.

Considering the facts that defects in a-Si:H can emit/capture an electron, i.e., to be oxidized/reduced and that there are mobile hydrogen species available, it is justified to state that a-Si:H exhibits

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