A Unified Model for Charge Defect Generation in a-SiH: Photo-Induced Defects in Photovoltaic (PV) Devices and Current Induced Defects in Thin Film Transistors (TFTs)

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1. Introduction

Defect generation occurs during operation of a-Si:H PV and TFT devices, and can be accelerated by stress testing. For both PV and TFT devices: i) densities of Si dangling bonds in undoped a-Si:H in (a) i-regions of p-i-n solar cells, and (b) channel regions of TFTs must be minimized, ii) contacts to these regions are by heavily doped amorphous or microcrystalline silicon, and iii) defect generation during operation as: (a) the Staebler-Wronski effect in PV devices, and (b) current-induced increases in threshold voltage in TFTs, involving H atoms, and in some instances also impurities such as O or NH. A unified defect generation model is presented for two-carrier PV devices and single carrier TFTs. Defect generation pathways are based on empirical chemistry, and then validated and quantified through ab initio calculations which have focused on reaction properties including their: i) exothermic character, ii) reaction barriers, and iii) transition state geometries. These calculations have been complemented by chemical kinetic calculations to quantify the effect of deuterium (D) for H substitutions in reducing defect generation rates. Calculations have been applied to intrinsic reaction pathways involving only Si and H atoms, and extrinsic pathways involving impurities such as O atoms and NH groups.

2. Defect Generation Reactions

Photovoltaic Devices

In device-grade a-Si:H light-induced defect generation is an intrinsic effect for impurity levels of O and N below ~5x1018 cm-3. Important experimental results are: i) prolonged light-soaking reduces dark-conductivity and photoconductivity [1], ii) light-soaking effects are completely reversible, iii) H atoms are not back-bonded to Si dangling bonds created by light-soaking [2], iv) light-soaking produces increases in IR absorption at ~2000 cm-1 equivalent to 1018 cm-3 'additional' Si-H bonds [3], iv) defect densities after light-soaking are increased to levels ≥1017 cm-3 [2], and iv) light-soaking rates are reduced by factors of 1.5 to 3 after D for H substitution in solar cell i-regions [4]. Defect generation occurs during recombination, or deep trapping so that both carriers are removed from conduction processes. This paper first treats reaction pathways for holes [5,6]. and then for electrons.

An extrinsic mechanism that can terminate hole transport involves the creation of positively charged oxonium (O_3^+) centers:

defect generation:
$$1h + {Si-H + Si-O-Si} --->$$

{ $(H-O-Si_2)^+ + Si^O$ }, and (1a)
defect neutralization: $1e + {Si^O + (H-O-Si_2)^+} --->$
{ $Si-H + Si-O-Si$ }. (1b)

The brackets {---} indicate the Si-H and Si-O-Si groups are nearest neighbors. Both reactions occur under light generation, and a steady state is reached in which (1a) dominates [6]. Since NH groups are isoelectronic to O atoms, equations analogous to (1a,b) apply for replacement of O with NH, where the positively charged defect is then a fourfold coordinated N atom (ammonium) with 2 Si and 2 H atom neighbors. Persuasive evidence for the NH reactions is from a-Si:N:H alloys prepared by remote PECVD. Using N2 and NH3 source gases, it is possible to produce alloys, either with and without NH groups [5,6]. Alloys with NH groups show defect generation greater by a factor of 5-6, consistent with differences in reaction kinetics for N initially bonded to 3 Si atoms, and N initially bonded to 2 Si and 1 H-atom [6]. Paralleling Eqn. (1), reaction pathways for an intrinsic defect generation process are given by:

defect generation:
$$1h + {Si-H + Si-Si} --->$$

{(Si-H-Si)⁺ + Si⁰}, and (2a)
defect neutralization: $1e + {Si0 + (Si-Si)^+} --->$
{Si-H + Si-Si}, (2b)

where Si--Si is a *strained* bond. Ab initio calculations show: i) reaction (2a) is exothermic by ~1 eV, ii) the reaction barrier is ~0.4 eV, and iii) the transition state separation between the stretched Si-H and positively charged Si-Si bond center is about 3.5 Å. These results are in agreement with other theoretical studies [7]. Additionally, i) Eqns. (2a) and (2b) display the required mestastability, ii) H-atom motion is displacive, consistent with reversibility; iii) consistent with Ref. 3, substitution of (Si-H-Si)⁺ for Si-H increases IR absorption at ~2000 cm⁻¹ since the IR effective charge for (Si-H-Si)⁺ is larger by a factor of 3-4 than that of Si-H: abinitio calculations show the stretching mode of (Si-H-Si)⁺ is at ~2000 cm⁻¹, and iv) consistent with the primary kinetic isotopic effect, reaction (2a) will be retarded by at most 3 when D is substituted for H. Finally, the stability of the body-center bonding arrangement $(Si-H-Si)^+$ is consistent with the reported stability of bond-centered positively charged muons, μ^+ , in a-Si:H [8]. Similar reaction pathways apply for generation of negatively charged defects by electron trapping. For example, Eqns. (3a) and (3b) give reactions for an extrinsic pathway involving bridging O atoms:

defect generation: $1e + {Si-H + Si-O-Si} = -->$ {(H-O-Si) + Si⁻ + Si⁰}, and (3a) defect neutralization: $1h + {(H-O-Si) + Si⁻ + Si⁰} = -->$ {Si-H + Si-O-Si}. (3b)

This mechanism is also supported by the ab initio calculations. Eqn. (3a) is based on initially trapping a photogenerated electron in the anti-bonding orbital of an Si-H group. Hydrogen bonding between H of the Si-H and the neighboring O atom then promotes a displacive motion of the H. Similar extrinsic reaction pathways apply for iregions with NH groups. Finally, ab initio calculations have also helped to identify to an intrinsic pathway involving only Si and H. This pathway is essentially the same as what is discussed below for the TFTs (see Eqns. (5a,b).

Thin Film Transistor Devices

Negatively charged defects are generated in the channel regions of TFTs after high levels of current stress [9]. As noted above, there is an important distinction between lightinduced defect generation in PV devices and current induced defect generation in TFTs. In PV devices, hole-electron pairs are created by optical absorption, and a microscopic description must explain recombination (or deep trapping) of both holes and electrons [10], whereas in accumulation mode TFTs, defect generation is initiated by electrons, and only negatively charged defects can be generated because of surface band bending [9], Extrinsic and intrinsic pathways are based on changes in bonding produced initially by trapping of electrons in anti-bonding states of Si-H groups, and then followed by displacive H atom motion and bond restructuring. Pathways have been studied by ab initio calculations which confirm their exothermic nature. The proposed mechanisms are similar to those discussed in Ref. 9 for intrinsic processes; however, Ref. 9 does not address extrinsic processes, nor does it employ ab initio calculations to validate proposed reactions. The pathways for an extrinsic reaction involving O impurities are given by:

trapping:
$$1e + \{(Si-H) + Si-O-Si\} \dots \}$$

{Si⁻ + Si-OH-Si}, (4a)
defect stabilization: $1e + \{Si^- + Si-OH-Si\}$

$$---> \{2Si^{-} + (H-O-Si)\}.$$
 (4b)

The H atom of the Si-H group and the O-atom of the Si-O-Si group interact electrostatically forming a weak three center - two electron H-bond. Initial electron trapping takes place in an anti-bonding state of the Si-H group, and an overcoordinated neutral O is formed. This configuration is unstable and relaxes as shown in Eqn. (4b). Eqn. (5) gives an analogous pathway for an intrinsic process:

trapping :1e + {(Si-H) + Si-Si} --->
{Si⁻ + Si-H-Si}, (5a)
defect stabilization: 1e + {Si⁻ + Si-H-Si} --->
$${2Si- + (Si-H)}.$$
 (5b)

The net effect of Eqns. (5a,b) is to eliminate a strained Si--Si bond and produce two negatively charged dangling bonds. The transition between extrinsic and intrinsic behavior will depend on the dangling bond density in the as-deposited a-Si:H channel material. This is about 5×10^{15} cm⁻³ for device-quality a-Si:H, so that the transition between intrinsic and extrinsic behavior defect generation occurs at impurity levels of O and NH of ~1 to 5×10^{18} cm⁻³, similar to PV devices.

3. Summary

This paper has presented a unified model for defect generation in a-Si photovoltaic and thin film transistor devices. Defect generation involving both positively and negatively charged defects has been considered for the PV devices, and defect generation involving only negatively charged defects has been considered for the TFT devices. Proposed defect generation reactions are intrinsically metastable, and are charged carrier induced. Reaction pathways have been verified by ab initio calculations on relatively small clusters, but the agreement between calculated results and experiment is sufficiently good to justify this approach. Defect generation in the PV devices is reduced by D for H substitutions and similar results are anticipated for the TFT devices.

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