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Light Induced Metastability in Thin Nanocrystalline Silicon Films

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This paper examines the influence of light induced metastability on conduction in thin nc-Si:H films. To investigate the role of surface effects two sample types are considered: one with intentionally oxidised surface to form an oxide cap layer and the other with the oxide layer etched. Both Staebler-Wronski effect (SWE) and persistent photo-current (PPC) have been observed, albeit at different phases of light soaking (LS). For the nc-Si:H sample with cap layer, we attribute the presence of SWE and PPC to defect generation and interface charge trapping, while in the absence of the cap layer, these effects could be caused by unidentified photo-structural changes and defect generation.

Keywords: nanocrystalline silicon; light soaking; persistent photo-current; Staebler-Wronski effect

1. Introduction

The early 70s saw amorphous silicon (a-Si) as a low quality material with high defect density. All previous attempts to dope it had been unsuccessful because of the high defect density [1], therefore placing it in an impossible state from the standpoint of applications. However the technology was revolutionized when Spear and LeComber published their first results on the doping of a-Si with tri- and pentavalent elements [2]. They showed that by using hydrogen dilution during growth, high quality a-Si could be deposited. Soon after, Spear and collaborators demonstrated the first a-Si p-n junction with photovoltaic properties [3], pioneering an entire new area of a-Si solar cells. Later they also demonstrated the first working a-Si thin film transistor (TFT) [4], now widely used in flat panel displays. In summary, the efforts of Spear and his colleagues were a key factor that enabled a-Si to become a dominant technology for

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large area electronics, and which has led to notable developments in newly-emerging thin film materials such as nanocrystalline-Si (nc-Si).

The growth rate of nc-Si:H using RF plasma enhanced chemical vapour deposition (PECVD) is generally much lower than that of amorphous silicon (a-Si:H) [1], possibly due to the high hydrogen dilution required for nc-Si:H deposition. Furthermore thinner (less than about 50 nm) samples exhibit enhanced quantum confinement effects [6], which vanishes in thicker films because of increased grain size [7]. Enhanced quantum confinement offers additional properties, such as increased carrier mobility [8] which could have advantages when used in large area applications. For these reasons we examine thin nc-Si:H samples as they are attractive for use in electron devices such as thin film transistors (TFTs).

In amorphous silicon that has been subjected to light soaking (LS), both Staebler-Wronski effect (SWE) and persistent photo-current (PPC) have been observed. While SWE was observed in both the intrinsic and doped material, PPC was found only in the latter. The most pronounced feature of the SWE is the reduction of the dark conductivity after LS [9]. This is attributed to dangling bond (DB) generation as the result of tail to tail recombination during LS [10]. Other LS-induced effects such as change in the defect density, as measured by electron spin resonance (ESR) and constant photo-current (CPC), have also been observed. A number of models have been proposed to explain the mechanism of SWE. Most of the models are based on the change in the hydrogen and silicon bonds in the film [11].

It has been observed that incorporation of a silicon crystalline phase in the amorphous silicon matrix would reduce the SWE and hence slow the DB creation process [12]. A number of models have been proposed to explain this effect [13]. All the models are

based on the assumption that the defect generation takes place in the amorphous phase and the crystalline phase is stable.

Lubianiker et al. [12] argued that microcrystalline silicon incorporates two different types of amorphous phases; a highly defective, hydrogen rich amorphous silicon layer immediately adjacent to and surrounding crystalline grains, while further away is a higher-quality amorphous matrix. Photo carriers generated in the higher-quality amorphous phase during LS would recombine in the highly defective amorphous phase. This would result in a very small increase in the DB and hence slower SWE. Conversely, Kamei et al [14] proposed that the photo-generated carriers diffuse to the crystalline part due to the built-in potential as the result of the difference in band energies. Recombination in this case takes place in the crystal grains leading to a suppression of the non-radiative recombination in the amorphous region. This would lead to reduction in DB creation rate and reduce the SWE.

On the other hand, the PPC effect, traditionally observed in a-Si:H multilayers or porous Si [15], may be described by the potential barrier model for crystalline doping superlattices. According to this theory, the PPC in multilayers arises from photo-induced electron-hole pairs separated by the electric field at the p-n junction in superlattice. Because of the large spatial separation of charge carriers, the recombination lifetime becomes large. Porous silicon appears to show similar trends, since it is composed of small crystallites, and these introduce a fluctuation in the energy bandgap throughout the material [15]. Thus photo-excited carriers are spatially separated, which leads to an exceedingly long recombination life time.

Most of the conductivity studies on a-Si:H look at relatively thick films (typically 300 nm) to minimise the surface effects, whilst allowing for uniform absorption of light across the film [16]. Given that the structure of a-Si:H is independent of thickness,

this would constitute a valid measurement method for investigating bulk film conductivity, since the contribution of surface effects is negligible. However, it is known that the structure of nc-Si:H evolves with thickness, including surface roughness [17], grain size and crystal fraction [7], and consequently grain boundary interface area. Therefore conductivity studies of thick nc-Si:H films are not directly applicable to thinner films, because the results are strongly influenced by the surface effects and cannot be directly used for investigating bulk properties.

In this work we investigate light induced metastabilities of thin nc-Si films. We examine the conductivity while distinguishing between the influence of surface and the bulk. Most of the LS work on nc-Si has been on thick films [14][18], with thicknesses comparable to the i-layer used in solar cells. Furthermore the grain size of the sample used in this work was relatively small compared to other works [14]. Although there has been some work on the light induced metastability of nc-Si in p-i-n solar cells, these are fabricated in a sandwich structure such that current flows in a direction parallel to microcrystalline growth and therefore would pass through the amorphous incubation layer, and regions with gradually increasing crystalline fraction. Yue *et al* [19] showed that the solar cell degrades at different rates depending on bias conditions. It was argued that the difference in degradation rate was due to the recombination of photo-carriers taking place in the amorphous or highly crystalline phases, depending on bias. However in our work we look at planar structures where the direction of current flow does not have an impact on the light induced degradation.

2. Sample Preparation and Experimental Setup

Nc-Si:H samples used for this study were deposited at 280°C substrate temperature in a multi-chamber 13.56 MHz PECVD system from MVSystems. The nc-Si:H was deposited using a H_2 diluted SiH_4 plasma (H_2:SiH_4=100:1) at 900 mTorr chamber pressure. 50nm nc-Si:H film was deposited on a Corning 1737 substrate. The wafer was allowed to cool in a laboratory atmosphere, from the deposition temperature (280°C) to room temperature (20°C) thus creating a thin oxide cap layer. At this temperature and cooling rate, dehydrogenation is not expected to occur.

Then the sample was diced and one piece was left with oxide cap layer (sample I). A second piece was briefly dipped in hydrofluoric (HF) acid to remove the thin surface oxide layer (sample II). This ensures that both samples have essentially same characteristics, such as hydrogen concentration and thermal history, and are different only in surface termination. The samples considered here have a mean nanocrystallite diameter of 4-5 nm, as determined by X-ray diffraction. The optical bandgap of our nc-Si:H samples is about 1.9 eV as determined by measurement of optical transmission-reflection.

Electrical measurements were carried out using two coplanar electrodes with an approximate separation of 500 μm made by a colloidal solution of silver paste. The voltage applied was 100 volts and all measurements were done using a Keithley 4200-SCS. Throughout the measurements the samples were kept in a variable temperature vacuum chamber with a base pressure of 1×10^{-6} Torr to avoid further oxidation.

Light soaking was performed using heat filtered white light from a 50 Watt tungsten-halogen lamp. The intensity of the light on the sample was 45 mW/cm^2. During the experiment the properties of the sample were investigated using sub-bandgap light. This was done using the same light source filtered by crystalline silicon wafer (i.e. $h\nu \leq 1.1$ eV).

3. Results

The effect of successive light exposures on the nc-Si:H sample with oxide cap (sample I) at room temperature is shown in Fig. 1. The light was turned on and off as indicated in the Figure. The duration of the light pulse was varied from 5 to 3600 seconds, while the dark current ($I_{d\text{-}LS}$) was measured for 5 minutes in-between successive exposures. Upon light exposure, we observe a fast rise in photo-current (I_{ph}), followed by a fast decrease after the illumination period, with a non-monotonic dependence of $I_{d\text{-}LS}$ on the exposure duration. Here $I_{d\text{-}LS}$ first decreases, but for longer exposures it starts to increase. Interestingly, for light exposures longer than 10 min, we note that the excess dark current (i.e. when $I_{d\text{-}LS}>I_{d\text{-}A}$) is persistent and does not relax to state A. This excess dark current is referred to as the persistent photo-current.

The effect of successive light exposures on the nc-Si:H sample without oxide cap (sample II) at room temperature is shown in Fig 2. The dark current in state A is higher by an order of magnitude compared to the oxide cap counterpart. In this case, the dark current increases after exposures of up to five minutes, indicating PPC. For longer exposures (~2 hrs), however, we observe that SWE becomes dominant. Annealing at 150°C for 1 hr was necessary to restore the sample to state A.

The temperature dependence of dark current in the annealed and light soaked states for the sample with the oxide cap is shown in Fig 3. Curve A shows the temperature dependence of dark current in the annealed state A, yielding an activation energy E_a = 0.45 ± 0.03 eV determined in the 300-400 K range. Curve SWE denotes the temperature dependence of dark current after 5 min of continuous exposure, which yields E_a = 0.60 ± 0.02 eV. The SWE is annealed out at 370 K. Curve PPC shows the temperature dependence of current after continuous light exposure for up to 1 hr. The

dark current in the PPC state initially increases, then decreases from 320 K before increasing again from 340 K. The activation energy for the annealing process from room temperature to 320 K is 0.23 ± 0.02 eV, and in the range 344 K to 415 K it is about 0.80 ± 0.02 eV.

The temperature dependence of the dark current in the annealed and light soaked states for the HF-etched sample is shown in Fig. 4. Curve A shows the temperature dependence of the dark current in the annealed state A yielding an activation energy E_a = 0.54 eV, determined in the range of 300-450 K. Curve PPC traces the temperature dependence of current after continuous light soaking up to 2 min. The PPC state is annealed out at about 410 K, yielding an activation energy E_a = 0.45 eV. The curve SWE, which denotes the temperature dependence of dark current after continuous exposure of 2 hrs, yields an activation energy E_a = 0.62 eV. Table 1 summarizes the various findings and extracted values.

4. Discussions

For sample I after short light exposures, the Staebler-Wronski effect (SWE) was found to be pronounced. In fact the decrease in dark current for short exposures is similar to the SWE in undoped a-Si:H. With increasing exposure time the PPC effect starts dominating. The same has been found in other structures, such as a-Si:H multilayers [20][21] and porous silicon [22]. When subject to sub-bandgap illumination, there is a transition between localized gap states or between localized and extended states, but no generation of free electron-hole pairs. Here we observe that PPC is partially quenched and does not return to the previous level after turning off exposure to sub-bandgap light.

The non-linear nature of the dark current, while annealing from PPC state, indicates a superposition of two effects. We believe that both PPC and SWE are simultaneously present while nc-Si:H is soaked with light for 10 min or more. A similar photo-current dependence for lightly boron doped a-Si:H sample has been reported by Aker and Fritzsche [23]. Here the PPC was attributed to charge trapping at the interface of a-Si and surface oxide. A similar explanation may hold in our case, following the findings of Halverson et al. [24] that light soaking creates hole traps, which are more prominent in the light soaked state rather than the annealed state A. This implies that charges trapped at interface defect states raise the electron quasi-Fermi level E_F. In fact there is a shift in Fermi level towards the conduction band edge after long exposures (curve PPC in Fig. 3), and the low annealing temperature of the PPC state in nc-Si:H indicates that the observed PPC could be caused by trapping of charge carriers at nc-Si:H/oxide interface. This is consistent with the fact that we cannot completely quench the PPC by exposure to sub-bandgap light. Note that the SWE is dominant for short exposures while PPC prevails for long exposures.

In contrast, for the sample without oxide cap, the PPC behaviour was recorded for short exposures and SWE for exposures greater than 30 minutes. Also when exposed to sub-bandgap light, the PPC was largely unaffected. Similar observations have also been reported for doping modulated a-Si:H multilayered thin films [20]. The relaxation time of PPC is many orders higher than the usual recombination time. To check whether the photo-current and excess dark current are controlled by the same mechanism, we measured the dependence of the photo-current on light intensity. The results appear to fit the function $I_{ph} \sim F^{\gamma}$, where F is the light intensity, and the exponent $\gamma \sim 0.6$. This value is quite similar for thin a-Si:H films. We therefore can conclude that the photo-current component is subject to the usual recombination-

trapping statistics. This is also in line with findings reported for doping modulated a-Si:H multilayered thin films [20].

The dark current increases by more than one order of magnitude in the HF-etched sample. The corresponding activation energies in the states A, SWE and PPC are also higher. A similar increase in activation energy on boron doped a-Si:H sample after HF treatment was observed by Aker and Fritzsche [23]. This could be explained by the shift of the effective Fermi level caused by the absence of holes at the nc-Si:H/oxide interface as a result of etching the negatively charged oxide layer [23].

The PPC effect reported here has many of the attributes predicted by the potential barrier model for crystalline doping superlattices. However, it can be annealed out only at sufficiently high temperature. This coupled with our inability to quench the PPC by sub-band gap light signifies that it is not caused by trapping of charge carriers in the mid-gap region (Fig. 4). Therefore a photo-structural change is most likely responsible in this case. On the other hand, the regular SWE is dominant for long exposures, and that causes a decrease in I_{DC} [25].

5. Conclusions

This work reported the light-induced metastability on conduction in thin nc-Si:H films. Both SWE and PPC effects were observed in oxide capped and HF etched nc-Si:H samples although at different phases of light soaking. With the former, the PPC was attributed to hole trapping at the oxide-Si interface, consistent with findings of Aker and Fritzsche. On the other hand, PPC in HF etched sample was found to be insensitive to sub-bandgap light, with higher activation energy, therefore indicating that some kind of structural changes are involved. The SWE observed in both cases is thought to be governed by the same mechanism as in a-Si:H. Although this is the first

time, to our knowledge, PPC has been observed in nc-Si:H, further experiments are needed to be able to decisively reveal the possible microscopic mechanisms underlying PPC. The metastable defects created by light soaking, have a non-monotonic effect on film conduction, which changes depending on the surface termination of nc-Si:H film.

Table 1. Summary of the results and discussions.

	Short exposure (< 10min)	Long exposures (>1hr)	IR exposure	Annealing at 330K	Mechanism for PPC
Oxidized nc-Si:H (Sample one)	SWE	PPC	IR quenches PPC.	Removes PPC.	Charge trapping at the nc-Si/oxide interface
HF treated nc-Si:H (Sample two)	PPC	SWE	IR is unable to quench PPC.	Does not remove PPC.	Unidentified photo-structural changes

Figure 1. Dark and photo-currents as a function of time of nc-Si:H before (state A), during, and after exposure to 45 mW/cm^2 heat filtered white light for successive exposures as indicated. Inset shows more clearly that the PPC state (color line) is quenched by sub-bandgap light. Dotted line corresponds to the annealed state guided to the eye and short-dotted line corresponds to dark current after LS.

Figure 2. Current of HF treated nc-Si:H as a function of time before (state A), during, and after exposure to heat filtered white light for increasing exposure times as indicated. Dotted line is indicated as the annealed state A and short-dotted line shows dark current after LS. Inset shows dark current and photo current before, during, and after exposure lengths of 1 and 2 min.

Figure 3. Effect of thermal annealing on dark current after continuous light soaking in the annealed state A, light soaked up to 1 hr (PPC state) and light soaked up to 5 min (SWE state) for sample with oxide cap.

Figure 4. Temperature dependence of the dark current in the annealed state A, PPC state (continuous light soaked up to 2 min) and SWE state (continuous light soaked up to 2 hrs) for the HF etched nc-Si:H sample.

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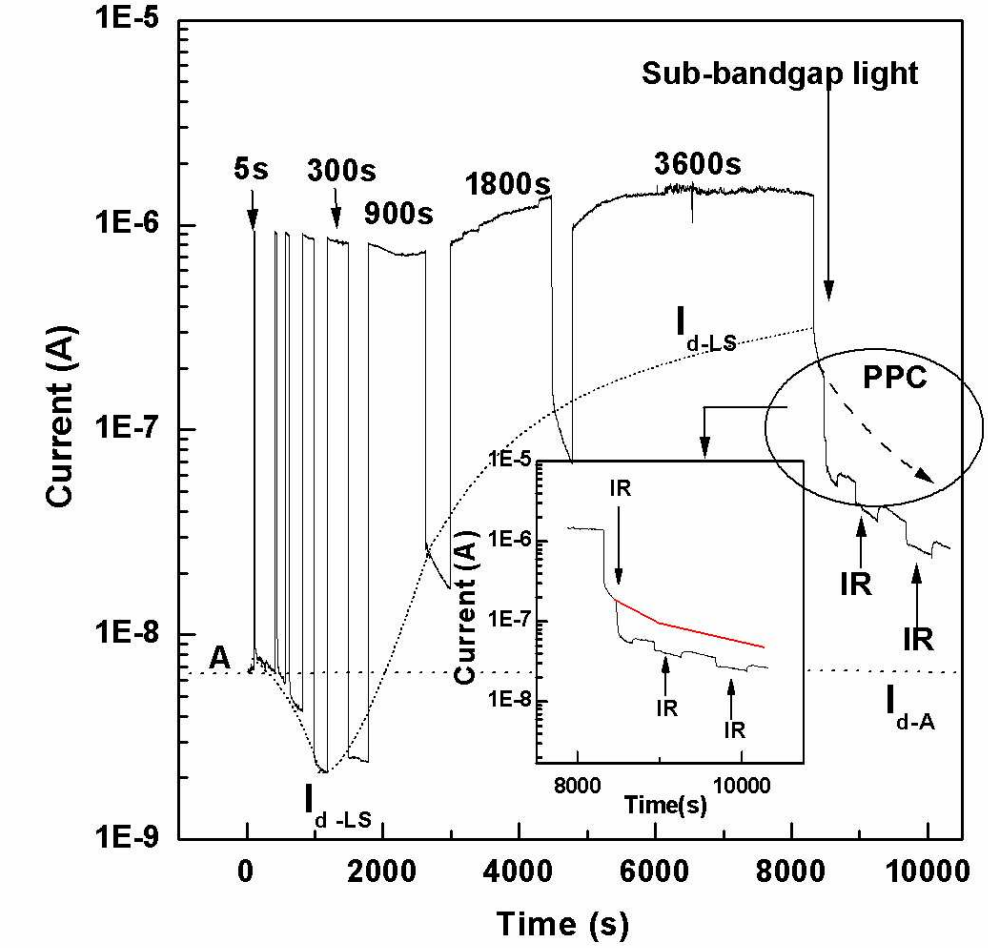

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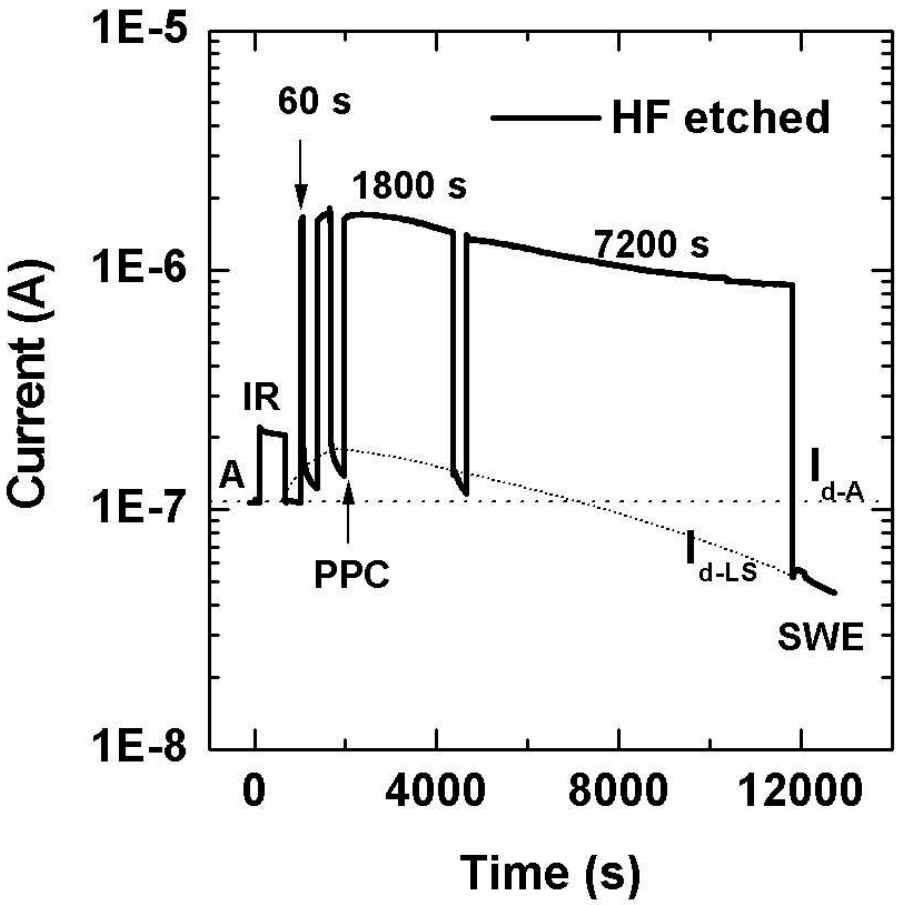

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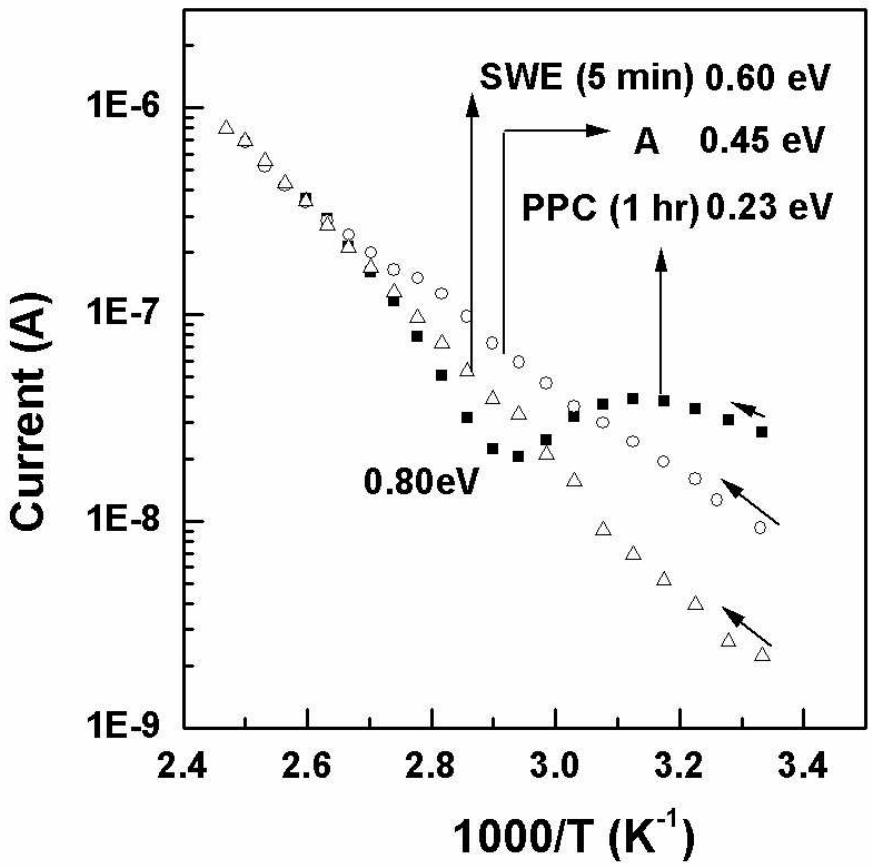

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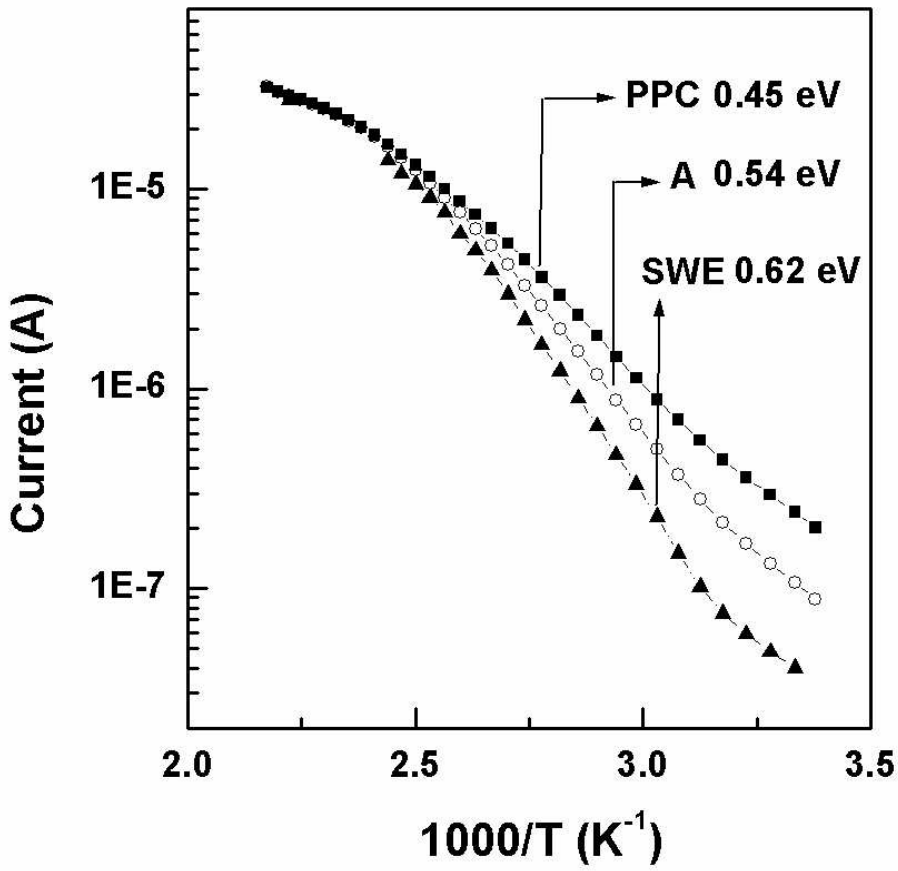

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