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High electric field photocurrent of Vidicon and diode devices using wide band gap a-Si:H prepared with intentional control of silicon network by chemical annealing

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Abstract

Wide band gap amorphous silicon (a-Si:H) were prepared by a chemical annealing (CA) technique, in which intermittent hydrogen plasma treatment was repeated during the deposition of a-Si:H. Electronic transport in the wide band gap a-Si:H at high electric field was investigated systematically using devices with Vidicon-type or n–i–p diode structures. The Vidicon-type image pick-up tube exhibited the potential to produce high resolution images, demonstrating that the wide-gap a-Si:H prepared by the CA had superior properties suitable for imaging devices. The electric fields as high as $>8\times10^5$ V cm^{-1} were applied successfully on the n–i–p devices using a-SiN:H for electron blocking contact. However, this electric field was not sufficient to invoke avalanche multiplication. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: a-Si:H; Band gap tuning; Chemical annealing; Structural relaxation; Avalanche multiplication; Vidicon

1. Introduction

So far, photoactive devices such as charge coupled devices (CCD) have been widely applied for image devices. However, increased demands to raise resolution and dynamic range in the imaging devices have required much improvements in sensitivity of the photoactive devices. Nonetheless, it is still a difficult subject to further improve the sensitivity in the CCD.

The discovery of the avalanche multiplication in amorphous selenium (a-Se) gave large impact [1] and enabled to develop very high sensitive image sensors which could be used in rather dark environments. This type of image devices has been referred to as ‘Avalanche Vidicon’, developed by Takasaki et al. and actually used in broadcasting, investigation and so on which need to take photography in night or dark places. However, the a-Se does not have enough thermal stability and less affinity with silicon technology.

Hydrogenated amorphous silicon (a-Si:H) shows higher thermal stability as well as higher affinity with silicon technology. Therefore, realization of the avalanche multiplication in a-Si:H have been a very attractive topic. There have been many attempts made to achieve avalanche multiplication in a-Si:H so far. Toyama et al. reported hot-electron-induced electro-luminescence [2] and described that avalanche multiplication was the most consistent explanation for this phenomenon. Sawada et al. observed the increase in primary photocurrent in p–i–n diodes at high electric fields ($\sim 9\times10^5$ V cm^{-1}) using a-Si:H for photoactive layer [3]. In addition, they developed novel staircase, stacked diode structures and observed the multiplication [4].

However, in all experimental results reported so far, there has not been enough evidence to conclude that these over gain currents were due to avalanche multiplication: i.e. the above results were obtained at rather low electric field and the response of photocurrent was rather slow. These data suggest that there remains the possibility that these over gain currents originated from secondary photocurrent injected due to the leaking at blocking contacts. Therefore, secondary current and/or leakage current should be suppressed.

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The most serious problem in the realization of avalanche multiplication is that it requires very high electric fields. Avalanche multiplication in a-Se occurred at a electric field of 1×10^6 V cm^{-1} or more [1], and the avalanche multiplication in a-Si:H may require equivalent electric field. However, typical band gap of a-Si:H (~ 1.75 eV) are not enough to apply such high electric fields because rather high dark conductivity originating from the narrow band gap usually results in break down at much lower electric fields than required for the avalanche multiplication.

We have developed a novel technique, referred to as chemical annealing (CA) technique, to tune band gap of a-Si:H from 1.7 to 2.0 eV [5]. These wide band gap a-Si:H showed low defect densities of the order 10^{15}/cm^3 and high photosensitivity larger than 10^5 S cm^{-1} under 100 mW cm^{-2} white light illumination. Also their Fermi levels are located in the middle of band gap and show very low dark conductivity ($\sim 10^{-13}$ S cm^{-1}) compared to those obtained with typical a-Si:H with band gaps of ~ 1.75 eV. The band gaps of these films are equivalent or wider than those of a-Se, and lead to low thermal carrier density. These features make the wide band gap a-Si:H prepared by the CA promising for imaging device applications including avalanche devices.

In this study, we prepared several devices using the wide band gap a-Si:H by the CA technique. Device structure was carefully optimized to apply high electric fields through suppressing leakage current for the realization of avalanche multiplication in a-Si:H. We investigated the leakage behavior of these devices from the evaluation of current–voltage characteristics at high reverse-bias voltages. Dc and ac photocurrent response measurements were employed to separate the contributions of primary and secondary photocurrents. Also the mechanism of leakage current at high electric fields is discussed in relation with device structures.

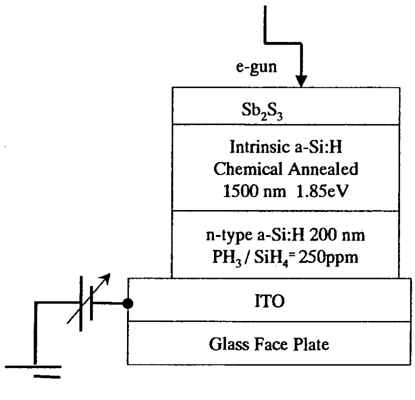

Fig. 1. A typical device structure of Vidicon type image pick up tube.

2. Experimental

Several devices were prepared by a capacitively coupled RF plasma enhanced chemical vapor deposition (RF-PECVD) apparatus [5] This system has two deposition chambers separated with a gate-valve, and samples can be transferred between both chambers without exposure to the air. This feature can avoid the air contamination at n | i or i | p interfaces.

The deposition chamber for intrinsic a-Si:H (i-layer) equips a microwave plasma generator to supply high flux chemically active species such as atomic hydrogen to tune band gap (Eg) of a-Si:H by the CA technique as reported previously [5]. In the CA procedure, SiH_4 and H_2 gas mixtures are supplied during growth period (the duration is referred to as t_1 (s)), and then the SiH_4 supply is stopped during the chemical annealing period (t_2). These periods are repeated to prepare thick i-layers (1.0–1.5 μm). The optimized condition to prepare high quality wide-gap a-Si:H with Eg of 1.85–1.90 eV are substrate temperature of 150°C, t_1 of ~ 80 s and t_2 of ~ 160 s.

Sb_2S_3 was used to form blocking contact for electron. It was deposited in a vacuum evaporation apparatus after exposure to the air. In some devices, p-type a-Si:H or non-doped a-SiN:H were used for electron blocking contact to examine the effect of electron blocking contact on current leakage behavior. For hole blocking contacts, n-type a-Si:H were used in all devices. These a-Si:H or a-SiN:H were prepared in another chamber of the multichamber apparatus using gas mixtures of SiH_4, H_2, NH_3, PH_3 and B_2H_6.

First, Vidicon-type image pick-up tubes were prepared using the wide-gap a-Si:H. The device structure is shown in Fig. 1. Gas phase doping ratio (PH_3:SiH_4) and thickness of n-layer are 250 ppm and 200 nm, respectively, which were optimized previously by Oda et al. [6]. Deposition of the Sb_2S_3 layer and the setup of other components for the Vidicion-type image pick-up tubes were made and the characterization was carried out by the assistance of Hamamatsu Photonics K.K.

Diode devices prepared in n–i–p sequence are also prepared for fundamental study of current–voltage (I–V) characteristics at high reverse-bias voltages (V_{bias}). In these devices, Ga-doped ZnO (GZO) coated glass substrates [7] were used for a window transparent electrode. The device structure is shown in Fig. 2.

I–V characteristics of these devices were evaluated by two techniques to study leakage current at high V_{bias} and break down electric field. One was conventional dc technique in which current density was measured at constant V_{bias} and steady-state illumination by ~ 400 nm LED monochromatic light (photon flux is $0.2 \sim 1 \times 10^{15}$/cm^2 s^{-1}). In addition, ac measurement using pulsed V_{bias} and illumination was employed to evaluate response time of photocurrent. Also this technique

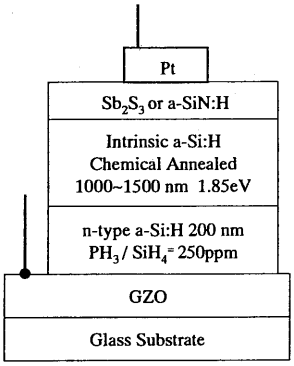

Fig. 2. A typical n–i–p device structure.

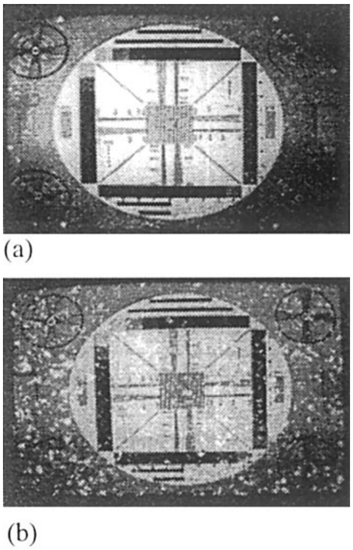

Fig. 3. Images produced by Vidicon type image pick up tube at bias voltage of -5 V (a) and -15 V (b).

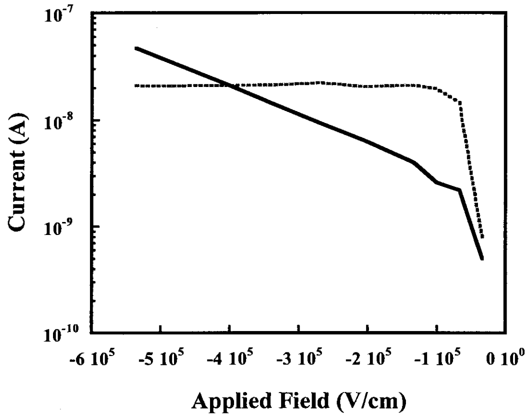

Fig. 4. Reverse *I–V* characteristics of Vidicon type image pick up tube. Black curve and dashed curve indicate dark current and photocurrent, respectively.

allows us to separate primary and secondary photocurrents from response behavior of current. Moreover, the employment of the ac measurement can limit the duration of high electric field application to very short period (~ ms), thus it is expected to reduce probability of break down at high electric fields and to increase actual breakdown voltage.

3. Result and discussion

3.1. Characteristics of Vidicon-type devices using the wide band gap a-Si:H

Fig. 3 shows the produced image by a Vidicon-type pick-up tube at V_{bias} of -5 V (a) and -15 V (b) (i-layer thickness was 1.5 μm). At a low V_{bias} of -5 V, a clear image is obtained with high resolution, demonstrating that the wide band gap a-Si:H has enough high quality to prepare high resolution, high contrast imaging devices. However, white spots appear at a higher V_{bias} of -15 V, implying that this wide band gap a-Si:H film contains in homogeneity and leakage current transiting through deteriorated areas of the film results in the appearance of the white spots. It was observed that the number of the white spots increased with increasing bias voltage.

Fig. 4 shows *I–V* characteristics of this Vidicon-type device. High photocurrent was maintained at high voltages up to 5.4×10^5 V cm^{-1} and there is no evident increase in the photocurrent with increasing V_{bias}, indicating that the observed photocurrent comes from primary photocurrent. In contrast, dark current increases proportional to the exponential of the V_{bias}. Taking the results of Fig. 3 into consideration, the path of this leakage current is thought to be the white spot areas. The Vidicon-type device was broken down at an electric field of -5.4×10^5 V cm^{-1} without any evidence of carrier multiplication, showing that this electric field is not enough to invoke the avalanche multiplication.

This result suggests that the leakage current must be suppressed to apply higher V_{bias} required for the realization of avalanche multiplication. However, the preparation of the Visicon-type device is quite time consuming process, thus we adopted simple n–i–p diode structures in the following study for fundamental study of leakage behaviors and improvement of break down voltage. The inhomogeneity of the wide band gap a-Si:H mentioned above was overcome by careful cleaning of the deposition chamber for the following studies with n–i–p diodes.

3.2. I–V characteristics of n–i–p devices measured by the dc and ac methods

In this section, n–i–p diodes were prepared using Sb_2S_3 layer. The thickness of the Sb_2S_3 layer was varied from 30 to 150 nm. Fig. 5 shows reverse-bias *I–V* characteristics of the n–i–p diode with 120 nm-thick

Sb_2S_3 layer. Dark current is very low ($\sim 10^{-10}$ A cm^{-2}) at low electric fields less than 10^5 V cm^{-1}, however, it exponentially increases with increasing reverse-bias electric field. The leakage behavior did not show significant dependence of the Sb_2S_3 thickness. Photocurrent slightly increases with increasing reverse-bias electric field unlikely to the case of the Vidicon-type device shown in Fig. 4. These results show that electron blocking contact made from Sb_2S_3 is not sufficient at these high electric fields.

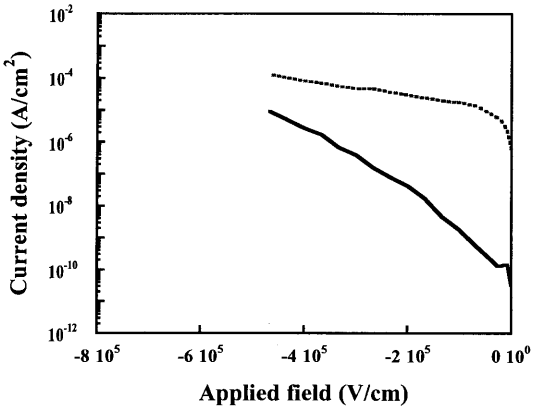

Fig. 5. I–V characteristics of an n–i–p diode device using Sb_2S_3 for electron blocking layer. Black curve and dashed curve indicates dark current and photocurrent, respectively.

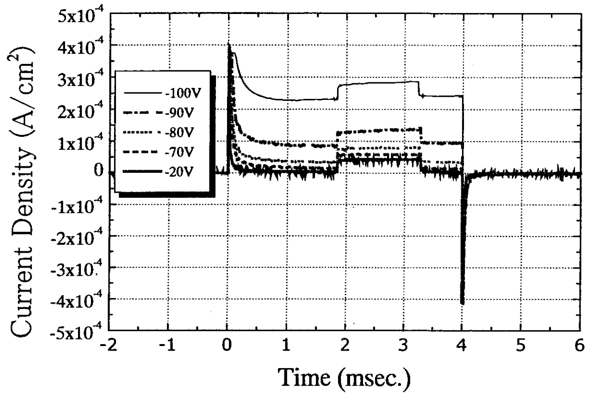

Fig. 6. Transient photocurrent signal measured by ac method. Numbers indicate applied voltage. i-layer thickness is 1500 nm in this case.

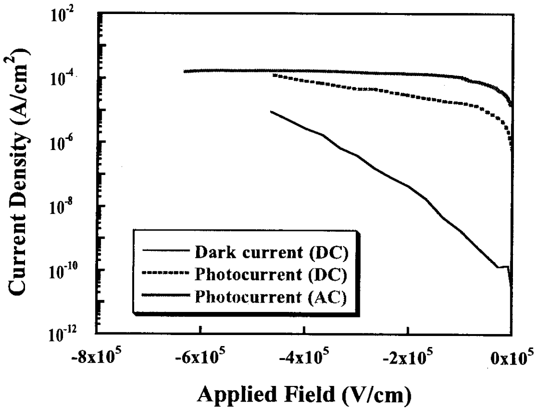

Fig. 7. I–V characteristics of a diode device using Sb_2S_3 for electron blocking layer. Solid gray curve indicates photocurrent measured by ac method. Dashed curve and solid black curve indicate dark and photocurrent shown in Fig. 4, respectively.

The leakage current is thought to include secondary photocurrent injected through the leakage at the blocking contacts not only primary photocurrent. Thus we next adopted the ac measurement. Fig. 6 shows time response of electric current in the ac measurement with a n–i–p diode with Sb_2S_3 layer (i-layer thickness was 1500 nm). In this case, pulsed V_{bias} varied from -20 to -100 V were applied during 0 and 4 ms, and pulsed light was illuminated between 1.8 and 3.2 ms. It shows that the photocurrent response time measured from the response after 1.8 ms is faster than the detection limit of the apparatus (< 1 μs). The response time of dark current when the electric field is applied at 0 ms is increased with increasing applied field and it is approximately 20 μs at an electric field of 6×10^5 V cm^{-1} (corresponds to 90 V). This slow response in dark current can be interpreted as the carrier injection to geometrical capacitance of the i-layer, however, it does not show such large V_{bias} dependence of response time. Thus this injection current contains the injection and carrier accumulation to n | i and/or i | Sb_2S_3 interfaces.

Fig. 7 shows reverse-bias I–V characteristics of the same diode as that shown in Figs. 5 and 6. Solid gray curve shows the photocurrent measured by the ac method. Dashed curves are the same as that of in Fig. 6 shown for comparison. It can be seen that the leakage of photocurrent at high V_{bias} measured by the ac method is well suppressed compared to the dc measurement case. And a higher breakdown electric field ($> 6 \times 10^5$ V cm^{-1}) is achieved than that obtained by the dc measurement (4.6×10^5 V cm^{-1}). Higher photocurrent than that of dc case is arisen simply from higher photon flux, and photon flux dependence of the breakdown voltage was not observed.

Further optimization of the device structure was carried out by employing a-SiN:H for an electron blocking layer instead of the Sb_2S_3, because a-SiN:H have demonstrated as the best insulator for a-Si:H thin film transistor and it can be prepared in the multichamber deposition system without the exposure to the air. Fig. 8 shows reverse-bias I–V characteristics of the diode using a-SiN:H. The thickness of a-SiN:H layer was optimized at 20 nm by preliminary experiments. Dark current is very low under electric fields less than 10^5 V cm^{-1}, however, it increases exponentially with increasing V_{bias} and exceeds the photocurrent at electric fields over 6×10^5 V cm^{-1}. In contrast, photocurrent is independent of V_{bias}. The photocurrent showed high response time less than the detection limit. These results clearly support the idea that the measured photocurrent

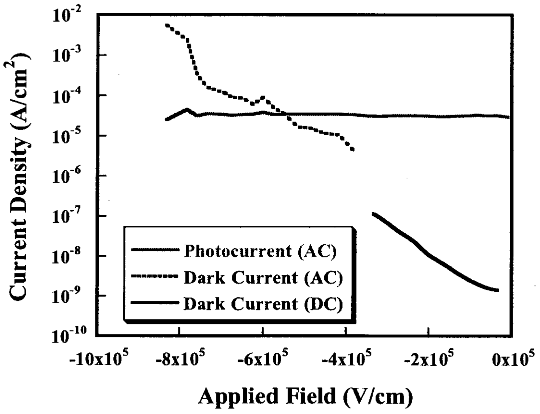

Fig. 8. Reverse I–V characteristics of a diode device using a-SiN:H for electron blocking layer. Black curve and dashed curve indicate dark current measured by dc and ac methods, respectively, and gray curve indicates photocurrent.

is primary photocurrent. This device structure successfully increases the break down electric field to $>8\times 10^5$ V cm^{-1}, however we could not observe the avalanche multiplication even at these electric fields.

3.3. Mechanism of leakage current at high reverse-bias electric fields

In this section, we discuss the origin of leakage current in detail. According to the Pool–Frenkel model [8], leakage current exponentially increases as a function of square root of electric field

$$I_{\text{leak}} = I_0 \exp\left(\frac{e\sqrt{V_{\text{bias}}}}{kT}\right)\left(\frac{-Ea}{kT}\right)$$

where I_{leak}, leakage current; I_0, constant; e, electron charge; k, Boltzmann constant; T, absolute temperature; Ea, barrier height at blocking contact, under the supposition that leakage current simply originates from reduction of the barrier height at a carrier blocking contact resulted from the increasing electric field. However, this is not the case for the n–i–p devices studied in this work since the leakage currents were exponentially proportional to V_{bias}, not to the square root. This indicates that the leakage mechanism does not follow the simple Pool–Frenkel model and we should incorporate more complicated leakage mechanism.

From the measurement of temperature dependence of leakage current, it was confirmed that activation energy was almost constant at ~ 0.9 eV at low electric fields below 4×10^5 V cm^{-1} and decreased with increasing V_{bias}. Activation energy of ~ 0.9 eV corresponding to a half band gap of a-Si:H i-layer indicates that carriers are excited to the conduction band of i-layer from the defect states located at near the middle of the band gap. The decrease in the activation energy with increasing V_{bias} can be explained from defect state distribution at interfaces. Interface defects are expected to distribute at various energy levels and act as traps for injection carriers. In this model, effective activation energy at interface region decreases with increasing V_{bias} as the increase in the number of carriers accumulated at interface defects raises the highest occupied defect state. This model suggests that reduction of the defect density at the interface is the most important to reduce the leakage current at high V_{bias}.

We should note that the Sb_2S_3 | i-layer interface was suffered from the air exposure before the deposition of Sb_2S_3 layer. These situations lead us to an idea that the leakage current at high V_{bias} for n–i–p diodes with Sb_2S_3 was caused by the defective Sb_2S_3 | i-layer interface. Thus we adopted a-SiN:H instead of the Sb_2S_3 because we can form clean a-SiN:H | i-layer interface without the air exposure. This resulted successfully in improved break down electric field up to $>8\times 10^5$ V cm^{-1}, however, the level of leakage current was not improved. One possible reason is that the deposition temperature was not optimized for good a-SiN:H | a-Si:H interface because the deposition temperature of the a-SiN:H was limited by that of the wide band gap a-Si:H which was very low 150°C. The possible solution of this issue is the employing of a-SiN:H | a-Si:H i-layer | n-type a-Si:H structure using optimized deposition temperature for a-SiN:H. In addition, there remains a possibility that the defect states at the n | i interface are also responsible for leakage current at high V_{bias}.

Generally, avalanche multiplication in a-Si:H needs electric fields greater than 10^6 V cm^{-1}. This work demonstrated that the ability of high field application of wide band gap a-Si:H prepared by the CA, however further optimizations of device structure are necessary to invoke the avalanche multiplication. This work could suggest that the improvement will be achieved by the optimization of n | i interface as well as the optimization of a-SiN:H | a-Si:H interface.

4. Summary

High quality wide band gap (Eg ~ 1.85 eV) a-Si:H were prepared by the chemical annealing. Several image pick-up tubes and n–i–p diodes were prepared using the wide band gap a-Si:H for i-layer, and high electric field transport in the wide-gap a-Si:H was studied. The Vidicon type image pick up tube produced clear images, exhibiting that the wide-gap a-Si:H has enough high quality for imaging device applications.

High electric field of 8×10^5 V cm^{-1} was applied successfully to the n–i–p diode devices. Even at this electric field, photocurrent showed saturation and short response time less than 1 μs, indicating that secondary photocurrent was negligible and response time is sufficiently short for imaging devices. The break down electric field was successfully improved to $>8\times10^5$ V cm^{-1} by adopting a-SiN:H layer for electron blocking contacts. However, this value is lower than that required for the avalanche multiplication in a-Si:H, and it could no be observed at these electric fields. Further optimization of device structure is necessary to suppress leakage current and to achieve avalanche multiplication.

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