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IMPROVED ELECTRICAL AND TRANSPORT CHARACTERISTICS OF AMORPHOUS SILICON BY ENRICHING WITH MICROCRYSTALLINE SILICON

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ABSTRACT

We have deposited n-i-p diodes with microcrystalline intrinsic layers for radiation detection applications. The diodes show interesting electrical characteristics which have not been reported before. From TOF measurement for our best samples we obtained $\mu E$ values which are about 3 times larger than our standard a-Si:H. For $\mu t$ values approximately a factor of 2 improvement was observed. The $N_{D}$ values derived from hole-onset measurements show lower ionized dangling bond density than normal a-Si:H material. We have proposed a simple model which can very well explain the experimental results.

INTRODUCTION

Since its first preparation through chemical transport technique by Veprek et al. in 1968 [1], microcrystalline silicon ($\mu$-Si) has been the subject of extensive research. Due to its low optical absorption and high electrical conductivity compared to hydrogenated amorphous silicon (a-Si:H), p-doped $\mu$-Si has been considered as window layers of solar cells [2-4]. Among different deposition techniques, the plasma CVD of H2 diluted SiH4 has been used more often. By PECVD it is possible to deposit microcrystalline material embedded in a-Si:H material with various degrees of crystallinity. A variety of deposition conditions have been studied by different groups for their effects on deposition rate, volume fraction of crystallinity, and crystalline grain size [5]. Although there are many reports on electronic properties of doped $\mu$-Si films, they deal mostly with dark and photo conductivity and bandgap measurement [6-8]. On electronic transport properties such as carrier mobility and lifetime, especially for undoped $\mu$-Si layers, direct measurement results are not available.

We are considering PECVD deposited $\mu$-Si -a-Si:H material (hereafter, just $\mu$-Si:H) for radiation detection applications. Our group, as well as others, have successfully used a-Si:H in the form of nip diode structures to detect charged particles, X-rays, gamma rays, and neutrons [9-10]. For these applications an important characteristic is the mobility lifetime product ($\mu t$) value, which determines the mean free path of charge carriers (d= $\mu tE$) within the intrinsic layer, that in turn controls the charge collection efficiency of the detector. In this paper we will present the measurement results on both material and electronic properties of our PECVD deposited $\mu$-Si:H samples.
Fig. 1 Typical transient photocurrent signals from the TOF measurement of: (a) electrons; (b) holes

EXPERIMENTAL

The samples we have measured were 5-8 \( \mu \text{m} \) thick nip diodes, deposited in our plasma enhanced CVD machine at an RF frequency of 85 MHz. For substrates we used Corning 7095 glass, and the top and bottom contacts were sputtered transparent Cr layers. The 300 nm thick n and p doped layers were deposited under our standard a-Si:H deposition conditions. We used hydrogen dilution only for the intrinsic layers. The deposition conditions for these layers are given in Table I. The sum of \( \text{H}_2 \) and \( \text{SiH}_4 \) flow rates were kept constant at 100 Sccm, while the flow rate ratios were varied for different samples. All samples were deposited at the pressure of 1Torr. The electron and hole mobilities were measured using the standard time of flight technique (TOF), by shining the p and n sides respectively. In our TOF experimental setup, we used a 3 ns (FWHM) \( \text{N}_2 \cdot \text{Dye} \) laser to produce 510 nm light (MPF~\( 0.2 \mu \text{m} \) in a-Si:H). Typical electron and hole photocurrent pulses are shown in Fig. 1.

For \( \mu \tau \) measurement, we used the same experimental setup and measured the collected charges for a set of reversed bias values. The data were then fitted to the Hecht equation [11] in order to derive the \( \mu \tau \) values.

The density of ionized dangling bonds (\( N_d^* \)) was determined by hole-onset measurement. In this measurement, laser light entered through the n sides of the samples and the signal amplitudes were measured by varying the reversed biases applied to the diodes. The onset voltage found in this manner was assumed to correspond to the full depletion of the device, and was used to calculate \( N_d^* \) from the appropriate equation.

RESULTS

The Microcrystalline structure of our samples was revealed by TEM images and micro diffraction patterns and was also confirmed by XRD spectra. Both TEM images and micro diffraction patterns showed Si microcrystals embedded in a-Si:H tissue (Fig. 2). The degree of...
Fig. 2 A TEM micrograph and the associated SAD for a µc-Si:H sample deposited at: H₂/SiH₄ = 25, Ts = 190°C, and P = 60 mW/cm².

Crystalline and the grain size depends on the deposition conditions. The grain sizes and crystallinity values are consistent with Ref. 5. In the XRD spectra of our various samples, a prominent peak at 2θ = 47.3 degrees shows that the materials are highly textured with a predominant (220) orientation (see Fig. 3). The same strong (220) orientation has also been reported in Ref. 12, for the µc-Si:H films deposited by layer-by-layer technique. Table II gives the results of electron and hole µ and µτ, as well as Nd* for our various samples for which the deposition conditions are listed in Table I. The last row gives the parameters of our standard a-Si:H material.

The measured electron and hole mobility values for these hydrogenated samples, as seen from Table II, depend on the deposition condition. For hydrogen to silane ratio of 15, sample MC361 shows to have an electron and hole mobility value of about 3 times larger than our standard a-Si:H. For the same sample, the µτ values for holes and electrons have improved approximately, by a factor of 2, compared to our normal a-Si:H values. These improvements either decreased or disappeared when higher temperature or higher power was used. At a hydrogen to silane ratio of 20, the sample produced at 190°C and 60 mW/cm² had improved overall characteristics for...
electrons, while for holes, only the mobility increased. The hole mobility for all samples deposited at lower temperature of 190°C showed an improvement by a factor of 2 to 3 over the standard a-Si:H values.

The \( N_p^* \) values derived from hole onset measurement are in general lower than our standard a-Si:H samples. For samples MC361 and MC363, the hole onset occurs at ~ 0 volts and the \( N_p^* \) values are estimated based on an assumed built-in potential of 0.9 volts.

In table II, we have also presented the results of our stress measurements. The stress values for the new samples are in general higher by a factor of 2-3 than standard a-Si:H.

**DISCUSSION**

Based on the measured data presented in table II, our \( \mu_c \)-Si:H samples deposited at optimum RF power and substrate temperature have electron and hole mobilities 2-4 times larger than our...
standard a-Si:H. The improvement in hole mobilities have also been reported by the Dundee group [8] for their microcrystalline samples deposited by microwave decomposition of H₂ diluted SiF₄. The fact that the increase in crystallinity by adding more hydrogen from the H₂/SiH₄ level of 15, or by using higher temperatures or powers did not result in any further enhancement in mobilities, but rather caused decrease in their values, leads us to believe that the higher mobilities are not the result of microcrystalline formations. But instead, it is the improvement in the quality of the amorphous material which is responsible for this favorable change. The hydrogen role can then be viewed as diffusing into the growing layers and breaking loose Si-Si bonds and therefore, enhancing the long range order in the amorphous material. This would imply narrower band tails, both at the conduction and valence mobility edges, resulting in higher drift mobilities for both electrons and holes. Using a simple geometrical model shows that, for the range of volume fraction of crystallinity that we are dealing with (<25%), a very small fraction of carriers would pass through microcrystallites. Thus, carrier mobilities are predominantly governed by the mobilities within the amorphous material (μₐ). Therefore, assuming that μₐ has improved, the increase in measured mobilities of the samples is well explained. We have also used a similar concept in order to simulate the effect of grain boundaries on the carrier lifetimes. Calculation of life time in the grain boundaries (τₐ) from this model, for both electrons and holes shows that as long as the ratio of grain size to volume fraction of crystallinity is less than 60, neither electron nor hole lifetime are appreciably affected by grain boundary captures. The increase in the measured μτ values of our best samples are in good agreement with the higher μ values and the model prediction of negligible or no adverse effect from grain boundaries on the overall carrier lifetime. For the overall defect density, due to the presence of grain boundaries, our model predicts a value about 10 times higher than the defect density of the amorphous part, while our measured values of ionized defect densities (N⁺) are better by a factor of 5-30 than that of normal amorphous silicon samples. The ionized dangling bond density, N⁺ from amorphous silicon samples is one third of the ESR measured N₀ value. Therefore, the lower values of N⁺ for our new samples may mean that, either the defect density in the amorphous part has improved by a large factor, or, for the new material, the relation between the N⁺ as measured by hole-onset method and the total defect density N₀ is different from the one established for standard amorphous silicon [13]. The former may be true, if we assume that the extra hydrogen also plays a role in passivating further some of the dangling bonds in the amorphous part. This is consistent with our stress measurement results which show about 2 times higher stress values for our new samples, and the empirically known inverse relation between the internal stress and the dangling bond density [14].

CONCLUSION

We have measured electron and hole μ and μτ for the new μc-Si:H samples deposited in our PECVD with high hydrogen dilution of silane. For the optimum deposition condition, we
measured mobility values ~3 times and $\mu\tau$ values approximately 2 times those of standard a-Si:H. The $N_D^*$ values have also improved. Stress measurements also show higher stress values. We have developed a simple model, the results of which are consistent with our measurements. We have suggested that these improvements might have come from the hydrogen dilution by suggesting the following roles for the extra hydrogen: a) it causes narrowing the band tails by breaking loose Si-Si bonds and therefore bringing about more long range order; b) passivating some more of the dangling bonds in the amorphous material.

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