

Infrared photoconductivity in heavily nitrogen doped a-Si:H

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ABSTRACT

High frequency steady-state photoconductivity in nitrogen doped hydrogenated amorphous silicon (a-Si:H-N) films has been demonstrated at infrared (IR) frequencies of 650 to 2000 cm^{-1} . This allows IR photoconductivity to be excited using a simple thermal source. In order to produce high frequency photoconductivity effects, the plasma frequency must be increased to the desired device operation frequency or higher as described by the Drude model. IR ellipsometry was used to measure the steady-state permittivity of the a-Si:H-N films as a function of pump illumination intensity. The largest permittivity change was found to be $\Delta\epsilon_r = 2$ resulting from a photo-carrier concentration on the order of 10^{22} cm^{-3} . IR photoconductivity is shown to be limited by the effective electron mobility.

INTRODUCTION

Thin film systems with IR conductivity or permittivity that may be actively tuned with the application of a DC electric field, have been of interest for some time to IR designers. As an alternative, photoconductive devices have been proposed for active IR systems. The carrier concentration can be actively changed by illuminating a-Si:H with source energy above the band gap and thus out of the IR band. This illumination results in the generation of electron-hole pairs, and a sufficient density of these carriers will result in a change in the material's permittivity in the IR frequency range. Thus, by varying out-of-band pump power, an active IR system may be achieved.

Photoconductive elements have been used for optically generated grid arrays and as switches for reconfigurable antennas at 40 GHz [1]. In these low frequency designs high resistivity Si wafers have been used as the photoconducting elements. Due to the nanoscale size of IR systems patterned a-Si:H thin films must be used for photoconducting elements, and a higher carrier concentration is required for a contrast in permittivity. The generated electron-hole pairs form a pseudo-metallic plasma with behavior described by the Drude model. Eq. 1 gives the permittivity of the photoconductive semiconductor as the difference between the dark permittivity $\epsilon_L(\omega)$ and a photo-plasma term

$$\epsilon_r(\omega) = \epsilon_L(\omega) - \frac{\omega_p^2}{\omega^2 - \frac{1}{\tau^2}} \times \left(1 + \frac{i}{\omega\tau} \right) \quad (1)$$

where ω_p is the plasma frequency, ω is the IR radiation frequency, and τ is the electronic relaxation time [2]. The plasma frequency depends upon the photo-carrier density in equation 2

$$\omega_p^2 = \frac{q^2}{\epsilon_0} \times \frac{n_{illum}}{m^*} \quad (2)$$

where q is the charge on the electron, ϵ_0 is the permittivity of free space, and m^* is the effective mass of the photo-carrier, and n_{illum} is the photo-carrier density as a function of power from the thermal pump source. n_{illum} should be greater than 10^{20} cm^{-3} for significant IR photoconductivity to occur.

THEORY

The photo-carrier density, n_{illum} , depends on the photon density, $G(P)$, and the recombination time, t , for electron hole pairs as shown in equation 3.

$$n_{illum} = G(P) \times t \quad (3)$$

The recombination time t is the average time required for electron-hole pairs to recombine thus eliminating the photo-carrier. For intrinsic a-Si:H t is on the order of a microsecond which means that for significant IR photoconductivity to occur $G(P)$ needs to be on the order of $10^{26} \text{ s}^{-1} \text{ cm}^{-3}$. By comparison a focused spot from a 100 W thermal source generates a $G(P)$ on the order of $10^{23} \text{ s}^{-1} \text{ cm}^{-3}$. Larger $G(P)$ values may be obtained using a pulsed source such as a strobe light, but this would result in non-steady-state photoconductivity. In order to make IR photoconductivity accessible with a simple thermal source, a slow t is required on the order of millisecond or longer.

Figure 1 shows density of state functions versus energy for intrinsic and n type a-Si:H.

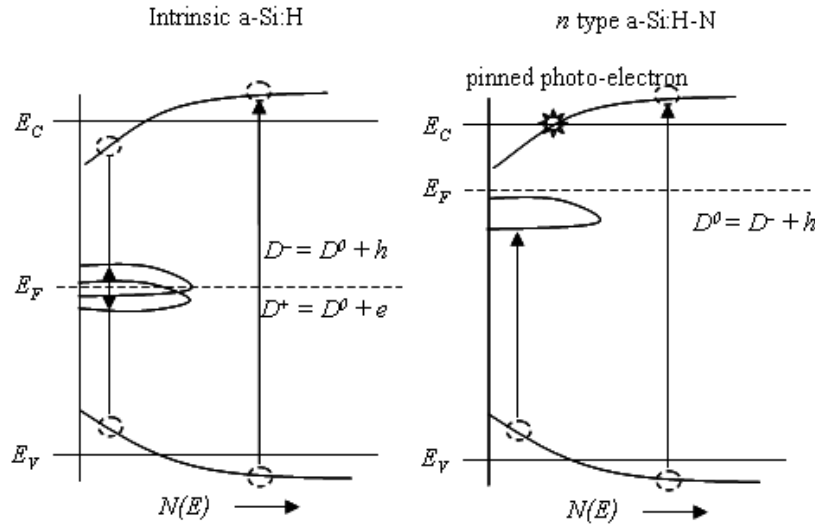


Figure 1. Density of states ($N(E)$) for a-Si:H.

In both cases E_C and E_V represent the energy of the mobility edge of the conduction and valence bands respectively while E_F is the Fermi energy. Near E_F in the forbidden gap of intrinsic a-Si:H are neutral dangling-bond states that may combine with electrons and holes to produce the charged dangling-bond defect reactions shown in the left half of Fig. 1. The production of charged dangling-bonds results in microsecond recombination

times for intrinsic a-Si:H [3]. With the addition of n type donors in the right half of Fig. 1 the Fermi energy increases, and this results in charged dangling bonds which quickly recombine with hole states. This results in a defect reaction that creates a neutralized dangling bond. An excess concentration of electrons is now present at the conduction level, and thus the photo-electrons may be said to be ‘pinned’ and left without hole states to recombine with. Doping with P has been observed to retard the recombination process in a-Si:H resulting in a high steady-state concentration of photo-carriers [4-5]. In order to pin electron-hole pairs the added impurity needs to be chosen such that the Fermi level of a-Si:H is increased. Nitrogen impurities can be expected to have a similar effect on the electronic structure as other group V elements, but even longer recombination times have been observed than in the case of P doping. For nitrogen concentrations in the range of 10^{20} to 10^{21} cm⁻³ the recombination time was measured to slow to between 10 and 100 ms [6] – enough to produce steady-state IR photoconductivity from a thermal source. This a-Si:H alloy is referred to as a-Si:H-N.

EXPERIMENT

Ion-assisted electron-beam evaporation was selected as the method for depositing a-Si:H-N thin films. Although evaporation is a less common method for a-Si:H deposition, it has been shown to successfully yield dense a-Si:H films suitable for photovoltaic devices [7]. Nitrogen is also added to the a-Si:H films via the evaporator’s ion source. Partial pressures of H₂ at a 25 sccm flow rate and a 99 % Ar balanced N₂ at 1 sccm were pumped into the chamber and ionized by a tungsten filament. The resulting plasma was maintained at a steady discharge current of 0.5 A. Simultaneously to the plasma formation Si was evaporated onto the sample at a rate of 0.5 nm/s.

The primary figure of merit for the a-Si:H-N films is the change in permittivity at IR wavelengths as measured by ellipsometry. In these experiments a J.A. Woollam Co. IR-VASE (variable angle spectroscopic ellipsometer) was used under standard *ex-situ* conditions. A test fixture was constructed to take ellipsometry data under illumination from a 12 V, 100 W quartz-halogen incandescent source. A high-pass filter is placed in front of the thermal source in the test fixture to block IR radiation so that the pump illumination is entirely out of band. The sample was constantly illuminated for 20 minutes during data collection.

The hydrogen concentration and Si-H bonding related microstructure may be evaluated using FTIR (fourier transform IR) spectroscopy. Nitrogen concentrations were measured directly using SIMS. The band gap energy, E_g , was measured using visible ellipsometry (J.A. Woollam Co. V-VASE), and E_g was found by fitting to a Lorentz-Tauc oscillator.

RESULTS AND DISCUSSION

Measured results are shown in Table 1 for three films selected because of their large photoconductive response. For the deposition parameters used the hydrogen concentration was in the desired range at around 10 at. %, and the nitrogen concentration was sufficient to slow the recombination time to around 100 ms based on comparison to

reference 6. The dark (n_{dark}) and illuminated carrier concentrations (n_{illum}) were based on comparing the generation rate and recombination time following equation 3, and then to DC secondary photoconductivity measurements. Due to the presence of localized states as shown in figure 1, the mobility is not constant for all states since carriers may exist on either side of the mobility edge. Equations 1-2 were used to determine an effective mobility for IR frequency transport by comparing the change in permittivity under illumination from the IR ellipsometry measurement to n_{illum} . It should not be assumed that the effective mobility for IR frequency transport is the same as the DC transport mobility. Even for metal films it has been shown that there is an effective mobility change at IR frequencies [8]. The effective IR mobility is about an order of magnitude smaller than the typical mobility for pure a-Si:H. Measurements of the DC carrier transport in references 10 and 6 were used to find n_{dark} and n_{illum} . DC carrier transport properties of a-Si:H-N were found to be similar to reference 6, and from comparison to reference 10, it can be seen that the carrier concentration is much higher than in pure a-Si:H.

Table I. Measured properties of a-Si:H-N with literature values for comparison. N_H and N_N are hydrogen and nitrogen concentrations, E_g is the band-gap energy, n_{dark} and n_{illum} are carrier concentrations under illumination, and μ^* is the effective IR mobility.

Sample	N_H , at. %	N_N , at. %	E_g , eV	n_{dark} , cm^{-3}	n_{illum} , cm^{-3}	μ^* , $cm^2/V-s$
hn02	20	2	1.6	5×10^{18}	2×10^{21}	0.76
hn03	6.6	1.2	1.4	4×10^{18}	5×10^{21}	0.56
hn12	28	2.8	1.62	2×10^{18}	2×10^{22}	0.18
a-Si:H [9]	10	0		2×10^8	2×10^{13}	
a-Si:H-N [6]	10	1.1		8×10^{18}	8×10^{21}	

Based on the high carrier concentrations and small effective mobility, equation 1 results in a nearly constant shift in permittivity. Due to the small mobility, the $1/\tau^2$ term is large compared to the frequency, so the change in permittivity is approximately equal to the squared product of the plasma frequency and relaxation time τ . Some spectral shifting of absorption features is also present as shown in Figs. 2-4. In figure 2 ellipsometry data of sample hn03 shows a change in permittivity of $\Delta\epsilon_r = 1.3$ to 2 across much of the measured spectrum. This is due to increased loss from the photo-carriers which can be seen by comparing the imaginary permittivity functions. Sensitivity to some loss features such as the Si-H stretching mode at 630 cm^{-1} begin to be screened by photo-carriers and no longer appear in the spectrum. This screening effect also occurs in sample hn02 which has a similar change in permittivity as shown in figure 3.

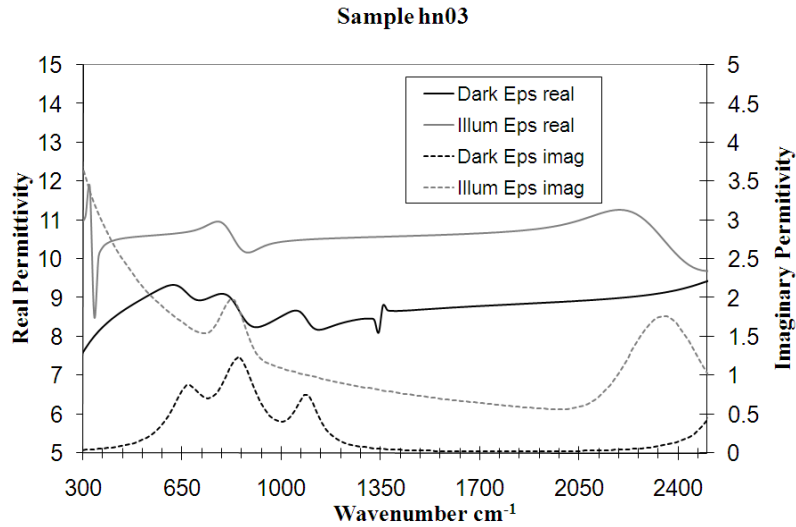


Figure 2. Real and imaginary portions of permittivity from ellipsometry measurements of sample hn03 in dark and illuminated state

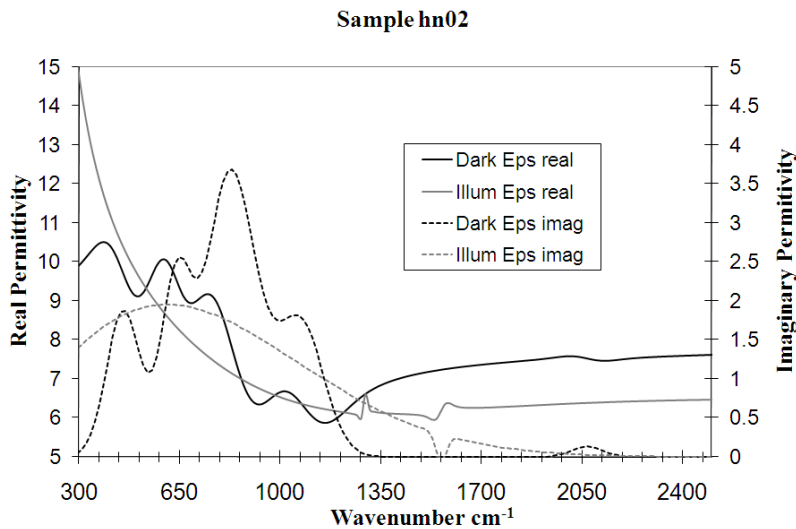


Figure 3. Real and imaginary portions of permittivity from ellipsometry measurements of sample hn02 in dark and illuminated state

Sample hn02 has both higher nitrogen and hydrogen concentrations than hn03, and as a result it also has stronger absorption features. This leads to a more pronounced photo-carrier screening effect. The change in permittivity under illumination was similar away from resonant features, and at frequencies greater than 1700 cm^{-1} $\Delta\epsilon_r = 1.5$. The change in permittivity achieved in samples hn02 and hn03 are the highest achieved in these experiments. Figure 4 shows results from sample hn12 which are typical of most the films produced.

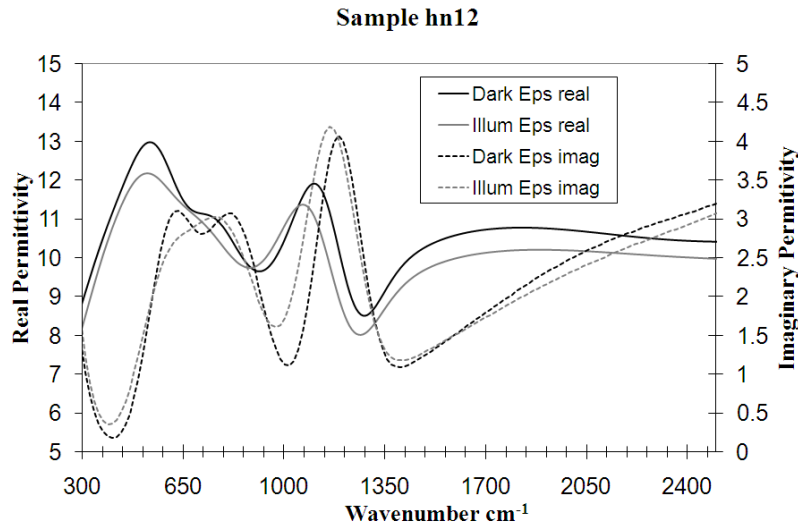


Figure 4. Real and imaginary portions of permittivity from ellipsometry measurements of sample hn12 in dark and illuminated state

The IR effective mobility of sample hn12 is smaller than hn02 and hn03 which results in a smaller change in permittivity where $\Delta\epsilon_r = 0.9$ away from resonance. IR frequency electron mobility is consistently the limiting factor in the permittivity change under illumination. Some photo-carrier screening is still present in sample hn12 as can be seen by the shifting of features in the imaginary part of permittivity, but the effect is smaller due to the limited mobility in hn12 compared to hn02.

CONCLUSION

Retarded electron-hole recombination in a-Si:H-N leads to high carrier concentrations suitable to create a change in permittivity under illumination at IR frequencies. This permittivity change is limited by the effective electron mobility at IR frequencies and is approximately equal to the product of the plasma frequency and the relaxation time. The largest permittivity change was found to be $\Delta\epsilon_r = 2$ and occurs over the spectral range from 650 to 2000 cm^{-1} .

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