

Amorphous Insulating Thin Films

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ANOMALOUS BEHAVIOR OF SEMI-INSULATING SILICON RICH AMORPHOUS SILICON NITRIDE

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ABSTRACT

Silicon rich PECVD amorphous silicon nitride has been used as an inter-level metal dielectric for making laser programmable connections on restructurable VLSI. There is an apparent Schottky barrier characteristic that has a 0.11 eV lower barrier for Ti than for Al. The stoichiometry was analyzed using RBS and HFS, and found to contain approximately 55% Si, 25% N, and 20% H by atomic percentages. The optical bandgap is 2.01 eV as found by the Tauc method.

The insulating behavior depends on time in an anomalous manner at applied fields greater than about 0.2 MV/cm, whereby the current increases with time for several seconds until it reaches an equilibrium value. The current decays in a normal charging manner at lower fields and in samples with insulating sub-layers between the electrodes and the nitride. When used as a gate dielectric, there is a long-time charging behavior that shifts the flat band voltage in the opposite direction of the applied stress. This shift is indicative of polarization within the dielectric. This behavior is similar to that of a reverse biased a-Si:H p-i-n diode.

INTRODUCTION

Amorphous silicon based compounds containing various elements including fluorine, carbon, and germanium have been proposed over the years to increase the thermal stability or to modulate the bandgap. Nitrogen incorporation has been shown to vary the band-gap smoothly from 1.75 to 5.5 eV [1]. Some groups have found that the photoconductive nature disappears when the ratio of nitrogen to silicon becomes greater than approximately unity, above which the band-gap opens sharply with increased nitrogen [2]. This material has also been used as a programmable anti-fuse material for high density laser induced metal-to-metal links [3].

A low concentration of nitrogen preserves many of the properties of pure a-Si:H, with a slightly wider band-gap [4]. An interesting feature of N incorporation is the apparent complimentary increase in hydrogen [5]. This becomes important for the reduction in dangling bond density, making the material possibly suitable for active, photosensitive devices. This possibility is further proven by the strong evidence that the hydrogen is mostly tied to silicon [6], making a minimum in the silicon dangling bond density for a low concentration of N [7]. A small concentration of N also suppresses the H evolution to approximately 500°C [8], demonstrating the stability of the alloy.

NITRIDE DEPOSITION

The films are a silicon rich a-Si:N:H alloy that were deposited in a load-locked single wafer plasma enhanced chemical vapor deposition (PECVD) system. The process chamber is a conventional parallel plate design powered by a 380 kHz RF generator through an automatic matching network. The substrates rested on the grounded lower electrode which was heated to 300° C. The gases were distributed through a heated showerhead

which served as the upper powered electrode. The chamber was cleaned with a CF_4/O_2 plasma after an accumulated deposition thickness of $6\text{ }\mu\text{m}$. The electrodes were pre-coated with the film to be deposited prior to deposition on the substrates. The system was pumped with dry vacuum pumps to remove any possibility of oil backstreaming and contamination of the films.

The silicon nitride films were deposited from $\text{SiH}_4/\text{N}_2/\text{NH}_3$ mixtures at 500 - 900 millitorr total pressure and 500 Watts RF (0.7 W/cm^3). Total gas flow was typically 4 SLPM resulting in a deposition rate of $5000 - 7000\text{ }\text{\AA}/\text{min}$ with an across wafer uniformity of $< \pm 3\%$. The nitrogen flow was 3500 sccm and the silane and ammonia flows were set to 420 and 250 sccm respectively. The film thicknesses and refractive indexes were determined by ellipsometry using a Rudolf Auto EL 4 at $6328\text{ }\text{\AA}$. For all the films, the refractive index was measured to be 2.43. Film compressive stress was determined to be approximately $9 \times 10^9\text{ dynes/cm}^2$ by measuring the curvature of films deposited on silicon substrates. The absorption spectra from 200 to 800 nm of films deposited on quartz were obtained using a HP 8452A diode array spectrometer to obtain the optical bandgap. The relative concentrations of Si, N and H were found by RBS and Hydrogen Forward Scattering (HFS) measurements to be .54, .24, and .21 respectively, and remained stable after a 30 minute sinter at 425°C .

ELECTRICAL PROPERTIES

The dark conductivity is very low ($< 10^{-14}\text{ }\Omega/\text{cm}$) at low fields, and the material is photo-conductive. The dark current was measured with samples between aluminum electrodes and is plotted on a Frenkel-Poole plot at several temperatures in Fig. 1 where the activation energy is seen to be $0.98 \pm 0.02\text{ eV}$ at the high field side. This value is close to half the optical bandgap of 2.01 eV derived from the photon absorption spectrum, using the Tauc method [9].

The same material was deposited in thicknesses of 400 nm and 700 nm between electrodes of Ti and Al. Fig. 2 shows the current versus voltage on a log-log plot. Both samples with Ti electrodes have greater current than their Al counterparts. The increased current with Ti electrodes is accounted for by a approximately 0.11 eV work function difference at room temperature, assuming a simple thermal activation energy. There is a distinct effect of the electrode, indicating that injection takes place in the high current regime.

At low fields, where the samples look highly insulating, the dielectric permittivity was measured at 100 kHz to be $9.0 \pm 0.5\text{ }\epsilon_0$. Independent of the electrode used, the nitride brakes down at a field of $1.9 \pm 0.1\text{ MV/cm}$, and the resistance after breakdown is ohmic and around $5\text{ }\Omega$, indicating that a metallic connection had been made.

To further understand the charging behavior, a series of charging and discharging experiments were performed on the $2400\text{ }\text{\AA}$ thick sample. A voltage was applied for 1000 seconds and then set to zero volts. The charging and then the discharging currents are shown in Fig. 3. The charging currents of Fig. 3a are in the positive direction, while the discharge currents of Fig. 3b are in the negative direction. The discharge current for voltages around 1 volt is close in form and in magnitude to the charging current, suggesting that most of the stored charge is recovered at low fields. The time scale for current changes with time is several hours for voltages $V < 2\text{ volts}$.

At higher voltages, the current decreases for a short time after which it increases again. This is anomalous behavior because the characteristics charging current is non monotonic for all values of applied voltage. The behavior resembles the long-time transient conduction observed in reverse biased a-Si:H p-i-n diodes [10]. This may be due to competing effects of injection as well as charging and discharging of deep trapping states.

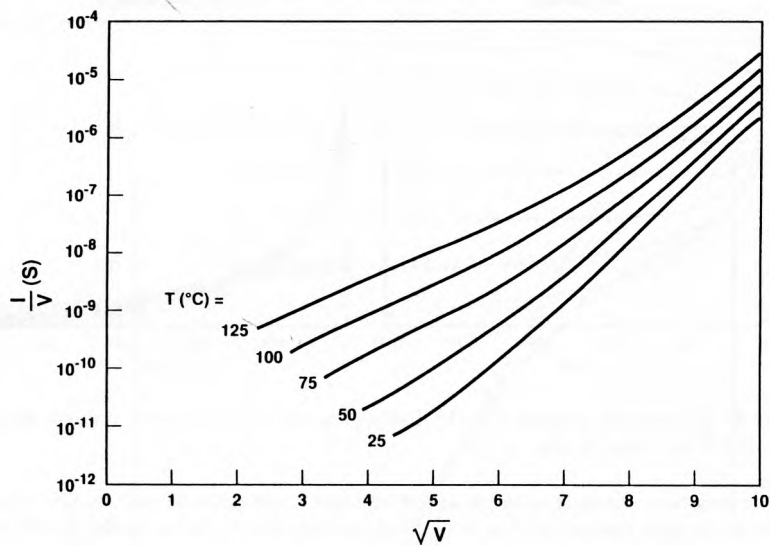


Figure 1: Frenkel-Poole plots of a 5800 Å thick nitride film at several temperatures. The area is $5 \times 10^{-4} \text{ cm}^2$.

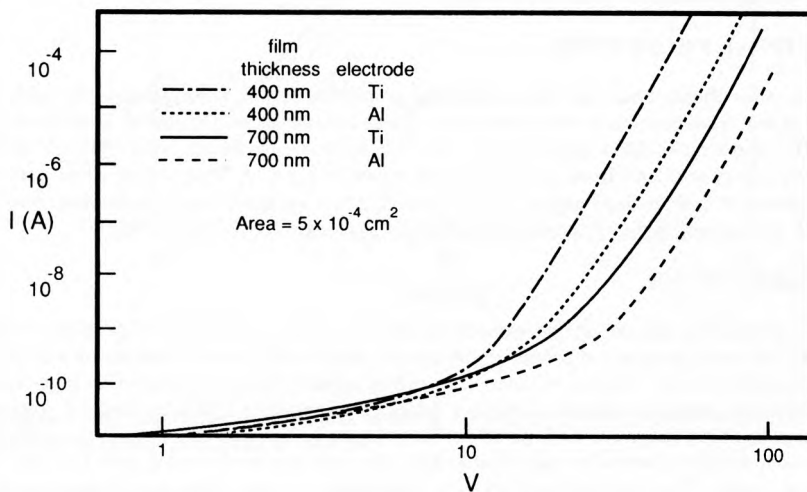


Figure 2: Log of current versus log of voltage for two thicknesses of nitride and two different metallization layers. The area is $5 \times 10^{-4} \text{ cm}^2$.

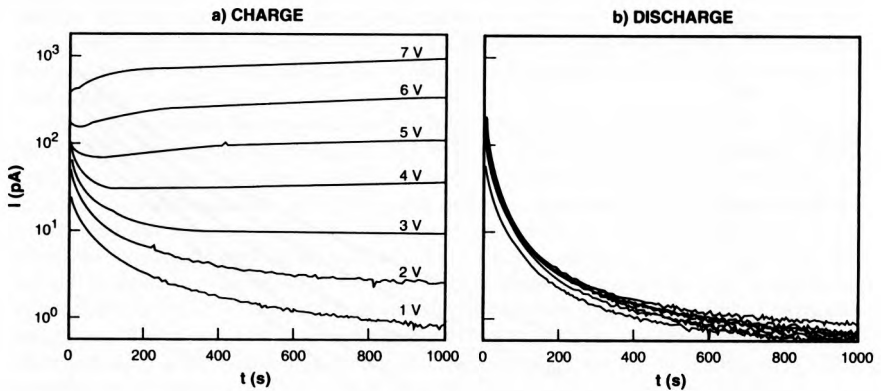


Figure 3: (a) charging currents and (b) discharging currents for several voltages applied to a 2400 Å thick nitride film.

The long-time charging behavior at low voltages is indicative of polarization charge. For field strengths that are too low to inject charge into the insulator, there is an effective increase in the very low frequency dielectric permittivity. Since the Si-N bond is not polar by nature and the band-gap is close to that of pure a-Si:H, it is possible that a concentration of negative correlation energy traps is responsible for this behavior [11]. The charge storage characteristics are similar to other studied silicon rich alloys [12]. The polarized charge decay can persist for several minutes allowing the possibility of fabricating an electret type memory cell.

OPTICAL PROPERTIES

To further characterize the semiconducting properties of this amorphous compound, a set of optical experiments were performed. These include Photo-Dispersive Spectroscopy (PDS) and time-of-flight experiments. The Urbach slope was found to be 140 meV with an E_4 energy at 2.2 eV from the PDS results shown in Fig 4. A Tauc plot of $\sqrt{\alpha h\nu}$ versus $h\nu$ gives a minimum band-gap of $E_T = 2.0$ eV. There is apparent band conduction as seen with the time-of-flight experiments which gives a $\mu\tau$ product of 3×10^{-10} cm²/V.

CONCLUSIONS

The silicon rich silicon nitride compound that has been used for laser programmable links has some unexpected properties by comparison to both amorphous silicon and stoichiometric nitride. At low voltages, the current appears to be dominated by long-time polarization, characteristic of an electret, which could sustain a field long after the voltage source has been removed. At high field, where electrode injection takes place, the current seems to be characterized by band conduction that depends on the metal work function of the electrode. The charging behavior may be explained by two competing charge transfer processes; polarization and injection. The polarization could result from positive and negative charge centers deep within the bands, distributed throughout the material.

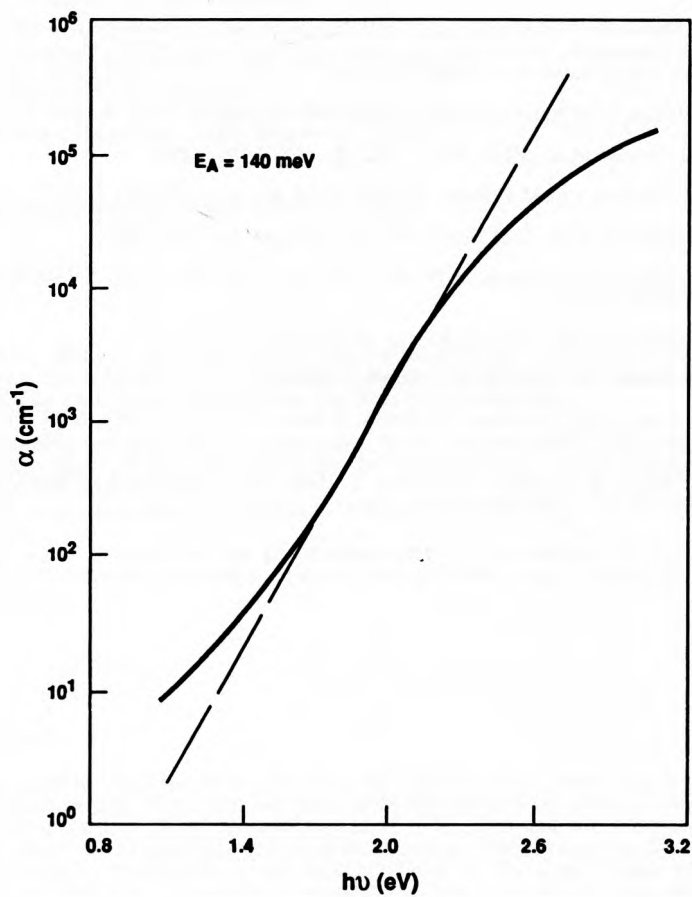


Figure 4: PDS spectrum on $\text{a-SiN}_x\text{:H}$, plotting the absorption versus photon energy; the tail has an exponential slope of 140 meV.

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