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Novel photosensor based on carbon nitride thin films

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ABSTRACT

Carbon nitride (C_3N_4) is gaining considerable research interest due to its unique electrical and optical properties. Herein, we report a sol-gel spin method for fabrication of Al/p-Si/ C_3N_4 /Au Schottky diode. The current–voltage (I – V) characteristics of the Schottky diode was investigated under dark and various light intensities. It was observed that the photocurrent of the Schottky diode increases with increase in light intensity. The transient photocurrent, capacitance, and conductance measurements were investigated. It was observed that the photocurrent, capacitance, and conductance highly depend on transient light. The photocurrent, capacitance, and conductance increases after illuminating the Schottky diode and returns to original value after turning off the illumination. The linear response of the photocurrent with light intensity suggests that carbon nitride based Schottky diode could be used as photosensor.

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1. Introduction

Carbon nitride (C_3N_4) is attracting considerable research interest after 1989 when Liu and Cohen presented a theoretical calculation showing some unique properties [1,2]. Based on their calculation, carbon nitride possess extremely high hardness, wide bandgap and large thermal conductivity. Additionally, carbon nitride is inexpensive, environmental friendly and can be synthesized using various methods [3–6]. Recently, Uddin et al. [7] have used sol-gel method to synthesize nano-crystalline carbon nitride thin films on stainless steel substrate using hexamethylenetetramine and urea. The hardness of the synthesized carbon nitride films was found to be 2.74–4.35 times higher than that of stainless steel.

The photo catalytic behavior of carbon nitride was studied using methyl orange as dye [8]. The photo catalytic behavior of carbon nitride was observed to improve by silver loading. The degradation rate of the methyl orange was further improved by the presence of strong acid radical ions. Dong et al. [9] has synthesized carbon nitride from an oxygen-containing precursor by directly treating urea in air between 450 and 600 °C, without the assistance of a template. It was observed that carbon nitride

has strong visible light absorption with a band gap of about 2.7 eV. It was reported that the crystallinity and specific surface areas of the carbon nitride increases with increasing heating temperature. Wang et al. [10] have used a facile method to synthesize nano porous carbon nitride using variety of block copolymers, nonionic surfactants, and ionic liquids as a soft templates. The pore size and specific surface area of the carbon nitride was tuned via controlling the template content and processing conditions.

In this work, for the first time we are reporting the photo response of carbon nitride film prepared using a sol-gel spin method. The current–voltage (I – V) characteristics of the diode prepared using carbon nitride was investigated under dark and various light intensities. The results indicated that carbon nitride is very sensitive to light and can be used as a photosensor diode.

2. Experimental details

Carbon nitride film was deposited on p-silicon wafer using a sol-gel spin coating method. Hexamethylenetetramine and urea were used as precursors for this coating. Prior to deposition of the carbon nitride film, the silicon substrate (600 μ m in thickness, 5–10 Ω cm resistivity, and (1 1 1) orientation) was chemically etched by the solution of HF for 1 min and then rinsed in re-distilled water using an ultrasonic bath for 10–15 min. The aqueous solution of hexamethylenetetramine and aqueous solution of urea (1:1 M) were

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mixed at room temperature and aged for 1 h. The resulting solution was spin coated (2000 rpm) on silicon wafer. After each coating, the deposited sol was dried at 150 °C for 10 min to obtain solid film. The coating procedure was repeated for 5 times. Finally, the substrate was heated at 600 °C for 30 min under N₂ atmosphere. After coating of the film, a circular top contact (area 3.14 cm²) was made by evaporating gold using physical mask. Aluminum as back contact on silicon wafer was coated using the same technique. The X-ray diffraction patterns of the synthesized film was recorded by Bruker Advance D8 X-ray diffractometer using 2θ–θ scan with CuKα (λ = 1.5405 Å) radiation which operated at 40 kV and 40 mA. Surface morphologies of the synthesized films were investigated using a JEOL 7001-F scanning electron microscope equipped with X-ray energy dispersive spectrometer (EDS). The electrical characterization of the diode was done using 4200 Keithley semiconductor characterization system. Photovoltaic measurements were executed using a 200 W halogen lamp. The light intensity of the lamp was controlled by change of the current across the lamp and the intensity of light was measured using a solar power meter (TM-206).

3. Results and discussion

The XRD pattern of the C₃N₄ film shows polycrystalline nature (ESI, Fig. 1S). The morphology and grain size of the C₃N₄ film was studied using SEM (ESI, Fig. 2S). The film shows grain like structure with average grain size of 40 nm. Uddin et al. have observed grain size of about 50–500 nm for C₃N₄ films [6]. The EDS analysis of the film confirms the presence of C and N (~3:4::C:N atomic ratio). The presence of Si and Au peaks (ESI, Fig. 3S) in the EDS is due to silicon substrate and gold coating (to avoid charging effect during imaging).

The current–voltage characteristics of the Al/p-Si/C₃N₄/Au Schottky diode were studied under dark and various light illuminations (Fig. 1). The *I*–*V* characteristics of the device shows non-linear behavior with rectification. As seen in Fig. 1, the forward bias current increases exponentially with the voltage confirming the Schottky type nature. The current–voltage characteristics of the Al/p-Si/C₃N₄/Au Schottky diode can be expressed as [11]

$$I = I_0 \exp\left(\frac{q(V - IR_S)}{nkT}\right) \quad (1)$$

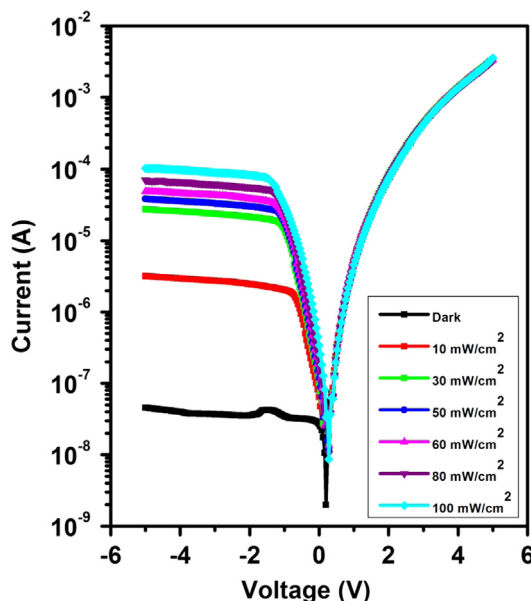


Fig. 1. *I*–*V* characteristics of the Al/p-Si/C₃N₄/Au Schottky diode under dark and various light intensity.

where *V* is the applied voltage, *q* is the electronic charge, *n* is the ideality factor, *k* is the Boltzmann constant, *T* is the temperature, *R_S* is the series resistance, and *I₀* is the reverse saturation current. The reverse saturation current *I₀* can be expressed as [12]

$$I_0 = AA^*T^2 \exp\left(\frac{-q\phi_b}{kT}\right) \quad (2)$$

where *A* is the active device area, *A** is the effective Richardson constant (equal to 32 A/cm² K² for p-type silicon) and ϕ_b is the barrier height [13]. The ideality factor is determined from the slope of the linear region of forward bias ln *I*–*V* plot. The barrier height of the device is calculated using Eq. (2). The ideality factor and barrier height of the diode were determined to be 2.24 and 0.65 eV, respectively.

Furthermore, it was observed that the current–voltage characteristics of the Al/p-Si/C₃N₄/Au Schottky diode strongly depends on the light intensity. The reverse bias current of the Al/p-Si/C₃N₄/Au Schottky diode increases with increase in the light intensity. Fig. 2 shows the variation of photocurrent as a function of light intensity. A linear relationship between photocurrent and light intensity suggest that Al/p-Si/C₃N₄/Au Schottky diode could be used as a photosensor [14].

The photo response of the Al/p-Si/C₃N₄/Au Schottky diode is quit evident from the *I*–*V* characteristics of the device. The increase in the current with light intensity was further explored using transient photocurrent study. Transient photocurrent measurements were performed by applying a constant potential across the device and by pulsing the light on the Al/p-Si/C₃N₄/Au Schottky diode from the top. The transient photocurrent with

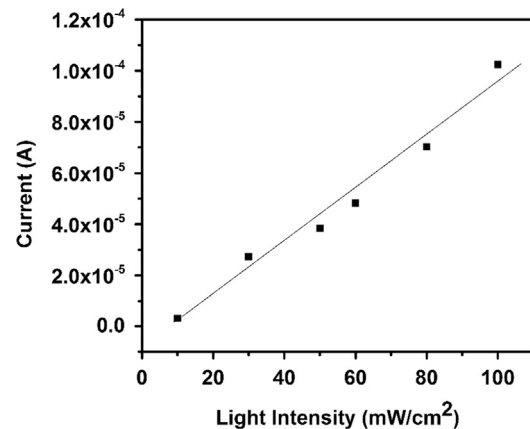


Fig. 2. Variation of photocurrent versus light intensity of the Al/p-Si/C₃N₄/Au Schottky diode.

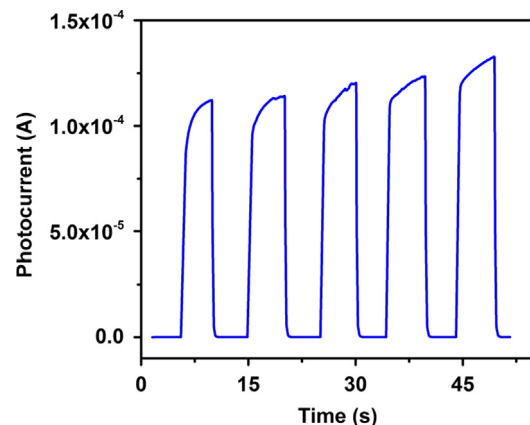


Fig. 3. Transient photocurrent measurement of the Al/p-Si/C₃N₄/Au Schottky diode.

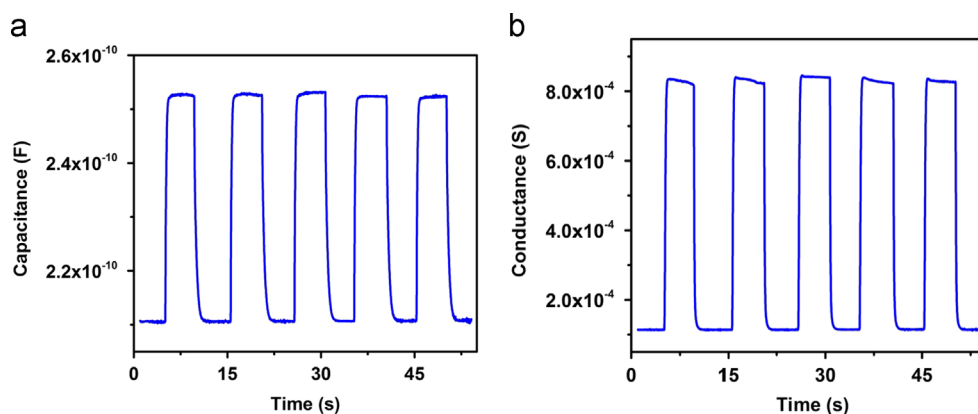


Fig. 4. (a) Transient photocapacitance and (b) photoconductance measurement of the Al/p-Si/C₃N₄/Au Schottky diode.

light on/off measurement as a function of time is shown in Fig. 3. As seen in the figure, the photocurrent of device increases sharply after illumination and reaches back to its original value after turning off the illumination. The initial rise in the current is due to generation of more free charge carriers on illuminating the device. On the other hand, the decay in the photocurrent after turning off the illumination is due to trapping of the charge carriers in the deep levels [15].

The photo-response of the Al/p-Si/C₃N₄/Au Schottky diode was further investigated by measuring transient capacitance and conductance. It is observed that the capacitance and conductance of the device strongly depends on the illumination. The transient photocapacitance and photoconductance measurements were shown in Fig. 4. As seen in Fig. 4, the photocapacitance and photoconductance of the Al/p-Si/C₃N₄/Au Schottky diode increases rapidly to a constant value after illumination the device and remains almost constant until the illumination is turned off. The initial rise in the capacitance and conductance suggests generation of more free charge carriers at junction on illuminating the diode. After turning off the illumination, the photocapacitance and photoconductance decreases to its initial value. The decay of the photocapacitance and photoconductance after switching off the illumination is due to trapping of the charge carriers in the deep levels. This behavior indicates that the Al/p-Si/C₃N₄/Au Schottky diode could be used as a photosensor.

4. Conclusion

In summary, for the first time we have investigated the photo-response of carbon nitride thin films. The *I*-*V* characteristics of the Al/p-Si/C₃N₄/Au Schottky diode depends on the light intensity. The linear response of current with light intensity suggest that the diode is photo sensitive. The photo response was further confirmed by transient photoconductivity measurement. The photocurrent, capacitance, and conductance was observed to increase after illumination, suggesting that carbon nitride could be used in photo sensing applications.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.matlet.2014.07.103>.

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