
Illumination Intensity Effects on the Dielectric Properties of Schottky Devices with Co, Ni-doped PVA Nanofibers as an Interfacial Layer

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ABSTRACT: In this study, the Au/poly(vinyl alcohol) (Co, Ni-doped)/*n*-Si Schottky devices (SDs) were fabricated using *n*-type single crystal silicon (phosphor-doped). The ohmic and rectifier contacts were thermally formed by annealing them in an evaporating system. Polyvinyl alcohol (PVA)/(Co-Ni) nanofiber film was used as an interfacial layer between metal-semiconductor. After the PVA/(Co-Ni) acetate was obtained, the nanofiber film was fabricated on silicon wafer using electrospinning technique. The dielectric properties of

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Au/PVA (Co,Ni-doped)/*n*-Si SDs were investigated in the gate voltage range of -1.5 to $+1.5$ V, before and after various illumination levels at 1 MHz. The dielectric constant (ϵ'), dielectric loss (ϵ''), dielectric loss tangent ($\tan\delta$), the ac electrical conductivity (σ_{ac}), and the real and imaginary parts of electric modulus (M' and M'') were obtained from the measured capacitance and conductance values. Experimental results show that the values of the dielectric parameters in dark and under illumination were different from each other. Also, these parameters were found to be functions of illumination intensity and gate voltage. Such illumination level-related behavior of dielectric parameters can be explained on the basis of Maxwell–Wagner interfacial polarization and restructuring and reordering of the charges at the interface states. © 2011 Wiley Periodicals, Inc. *Adv Polym Techn* 31: 63–70, 2012; View this article online at wileyonlinelibrary.com. DOI 10.1002/adv.20236

KEY WORDS: Au/PVA/*n*-Si, Dielectric properties, Polyvinyl alcohol

Introduction

Polymer and polymer composite nanofibers have been attractive materials for a wide range of applications because of their large surface area to volume ratio and the unique nanometer-scale architecture built by them.¹ Nanofiber is a fiber with diameter of nanometer order, less than 1 μm (more typically 50–500 nm), and the aspect ratio more than 100.² Nanofibers or nanowires provide a larger surface area per unit mass compared with that of films or bulk material. Therefore, they offer an opportunity to study the physical properties of one-dimensional structures as a subject of intense research because of their potential applications in many fields that include electronics, photonics, and sensing.^{3–10} Polymer composite nanofiber films can be produced by using electrospinning. This technique relies on electrostatic forces obtained by applying an electrical field by means of a dc high-voltage source between the tip of a nozzle and a collector. Electrospinning occurs when the electrical forces at the surface of the drop overcome the surface tension of the polymer solution. When this happens, the solution is ejected as an electrically charged jet and shoots towards the oppositely charged collector.

In this work, the Co, Ni-doped polyvinyl alcohol (PVA) nanofibers were produced by electrospinning. They were used in Schottky device (SD) fabrication as an interfacial layer. PVA as an interfacial layer was chosen because of its ease of processing, low cost, minimizing interface states of Schottky structures, and compatibility with Si. However, PVA is

normally a poor electrical conductor; it can become conductive by blending with some polymer. The poor conducting nature of PVA is thought to be due to the high physical interactions between the polymer chains via hydrogen bonding with the hydroxyl groups as well as the complex formation.¹¹ Thus, we can modify or improve the properties of PVA using reactions/interactions of the hydroxyl groups with other chemical compounds.¹² Especially, electrical properties of PVA are influenced not only by the structure and nature of a dopant, but also by the doping concentration and procedure.¹³ The incorporation of metal salts into polar organic polymers can induce pronounced changes in various properties of the polymers.^{14,15} The incorporation of metal salts, especially metal chlorides (CoCl_2 , CuCl_2 , and FeCl_3) into PVA produce intensity changes in infrared absorption bands of the polymers and result in a 10^6 -fold increase in the electrical conductivity of the films. Therefore, we doped PVA with Co and Ni composite materials.^{16–19} The fabrication of Au/PVA (Co, Ni-doped)/*n*-Si SDs is given in detail in the following section.

Experimental Procedure

In this work, the Au/PVA (Co, Ni-doped)/*n*-Si SDs were fabricated. Schematic cross section of the device is given in Fig. 1. The detail of the experimental procedure is explained step by step in the following section.

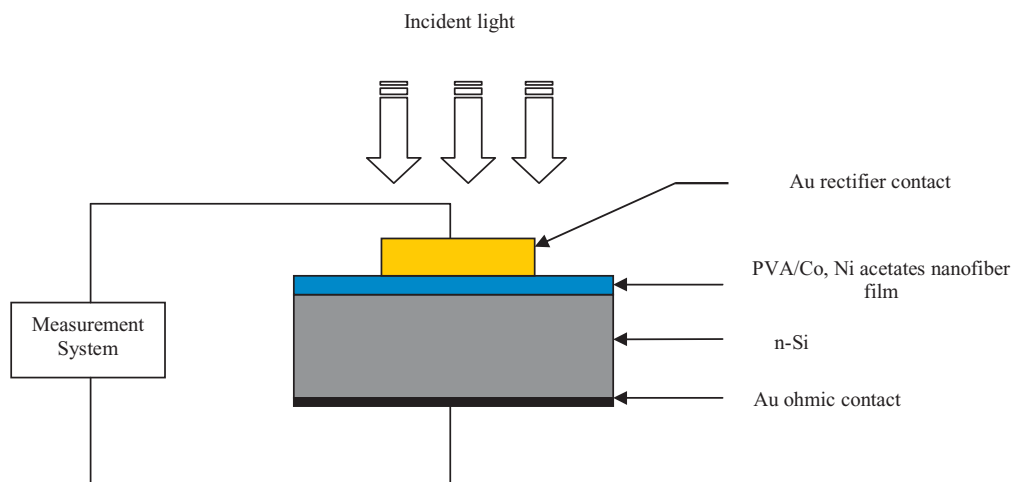


FIGURE 1. Schematic cross section of the device and measurement system.

FORMING OHMIC BACK CONTACT

The semiconductor used in this study was *n*-type (phosphor-doped) single crystal silicon (111) of thickness 350 μm and a resistivity of 0.7 $\Omega\text{-cm}$. For the initial fabrication process, Si wafer was degreased in an organic solution of peroxide-ammoniac in 10 min and then etched in a sequence of $\text{H}_2\text{O} + \text{HCl}$ solution, and finally quenched in deionized water for a prolonged time. Preceding each cleaning step, the wafer was rinsed thoroughly in deionized water of resistivity of 18 $\text{M}\Omega\text{-cm}$. Immediately after surface cleaning, high purity (99.999%) gold of thickness of approximately 2000 $\text{\AA}$ was thermally evaporated from the tungsten filament onto the whole backside of half wafer at a pressure of approximately 2×10^{-6} Torr, in oil vacuum pump system. The ohmic contacts were prepared by sintering the evaporated Au back contact at 450°C for 5 min in flowing dry nitrogen ambient at a rate of 2 L/min^{-1} .

PREPARATION OF PVA/Co, Ni AND SPINNING PVA/Co, Ni ON Si WAFER

0.5 g of cobalt acetate and 0.25 g of nickel acetate was mixed with 1 g of PVA, molecular weight = 72 000, and 9 mL of deionized water. After vigorous stirring for 2 h at 50°C, a viscous solution of PVA (Co, Ni-doped) was obtained. The conductivity of the PVA (Co, Ni-doped) polymer was measured $1.21 \times 10^{-6} \text{ S cm}^{-1}$ using four-point probe technique (ENTEK Company). The solution of the PVA (Co, Ni-doped) was homogenized by mixing with rota-

tion for 1.5 h before deposition. PVA (Co, Ni-doped) nanofiber film on *n*-Si substrate was coated by the electrospinning technique. Electrospinning process utilizes electrical force to produce polymer fibers. Electrospinning is especially interesting in that it is simple and cost effective. Electrospinning setup consists of four major components: the high-voltage power supply, the spinneret, the syringe pump, and the electrically conductive collector. A simple illustration of the electrospinning system is given in Fig. 2.

The composite solution for spinning was loaded into a 10-mL hypodermic stainless steel syringe with a needle (0.8 mm in diameter and 38 mm in length) connected to a digitally controlled pump (New Era), which provides a constant feeding rate. The positive electrode of a high-voltage power supply (SP-30P) was placed on the top of the needle. The negative electrode was connected to a metallic stationary collector wrapped with aluminum foil and served as a counter electrode, and spun under 20 kV. The working distance between the tip of the syringe needle and the collector was 19.5 cm. Composite fibers were collected on the Si wafer on the aluminum foil and dried at 60°C under vacuum for 10 h. The solvent evaporated and a charged fiber was deposited onto the Si wafer as a nonwoven mat. The fibers thus formed were dried in vacuum for 12 h at 80°C.

Fiber formation and morphology of the electrospun PVA/Co, Ni acetate fibers determined using a Scanning Electron Microscope (SEM) Quanta 400 FEI MK-2 (Czech Republic, brno) are given in Fig. 3.

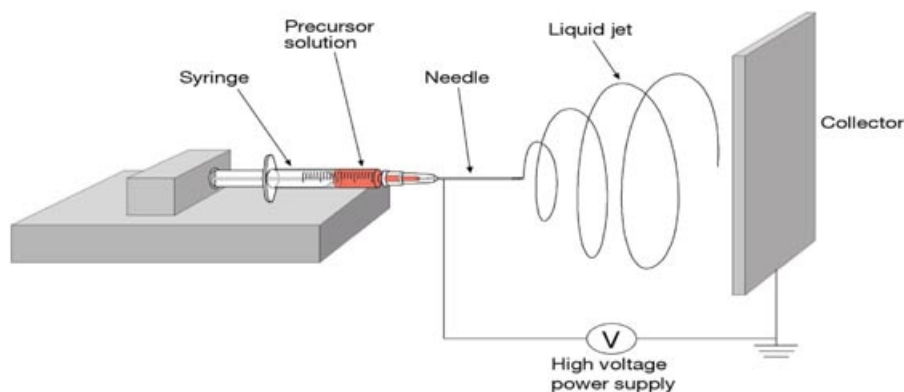


FIGURE 2. Schematic representation of the electrospinning process.

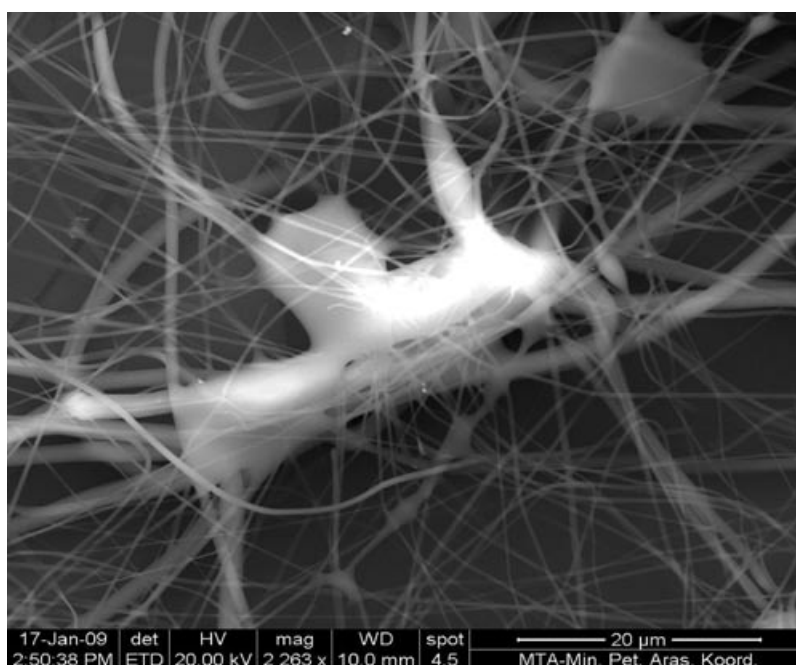


FIGURE 3. SEM images of PVA (Co, Ni acetates) nanofibers.

FABRICATING SCHOTTKY/ RECTIFIER CONTACT AND CAPACITANCE-CONDUCTANCE MEASUREMENTS

After the spinning process, Au circular rectifier contacts were coated by evaporation with a diameter of about 1.0 mm (diode area = $7.85 \times 10^{-3} \text{ cm}^2$). Figure 1 shows the typical device structure used in this work. The $C-V$ and $G/\omega-V$ measurements were performed in the dark and under various illumination intensities, at 1 MHz and room temperature, by using a HP/Agilent 4192A LF Impedance An-

alyzer, 5 Hz to 13 MHz (Santa Clara, US), and a small sinusoidal test signal of 20 mV_{p-p} from the external pulse generator is applied to the sample in order to meet the requirement. All measurements were carried out with the help of a microcomputer through an IEEE-488 ac/dc converter card (Industrial & Lab Automation with PCs ADVANTECH, CA). For illuminating the sample, a 250 W solar simulator (Model: 69931, Newport-Oriel Instruments, Stratford, CT) was used as a light source. The photons at different power levels passed through an AM1.5 (Model: 69931, Newport-Oriel Instruments), which allows wavelengths only between 400 and

700 nm, and reaches the surface of the devices. The intensity of the light was measured by research radiometer (Model ILT1700, International Light Technologies, MA).

Results and Discussion

The voltage dependence of the dielectric constant (ϵ'), dielectric loss (ϵ''), loss tangent ($\tan\delta$), ac electrical conductivity (σ_{ac}), and the real and imaginary parts of electric modulus (M' and M'') were evaluated from the knowledge of C and G/ω values of Au/PVA(Co,Ni-doped)/ n -Si SDs under various illumination intensities at room temperature and 1 MHz. The complex permittivity can be written^{20,21} as

$$\epsilon^* = \epsilon' - i\epsilon'' \quad (1)$$

where ϵ' and ϵ'' are the real and the imaginary components of the complex dielectric constant, respectively. The complex permittivity formalism has been employed to describe the electrical and dielectric properties. In the ϵ^* formalism, the real and the imaginary parts of the complex dielectric constant can be written^{22,23} as

$$\epsilon' = \frac{C_m}{C_0} \quad (2)$$

$$\epsilon'' = \frac{G_m}{\omega C_0} \quad (3)$$

where C_0 is the capacitance of an empty capacitor. $C_0 = \epsilon_0(A/d)$, where A is the rectifier contact area in cm^2 , d is the interfacial layer thickness, and ϵ_0 is the permittivity of free space charge ($\epsilon_0 = 8.85 \times 10^{-14} \text{ F/cm}$). The calculations are partly based on the illumination dependent measured capacitance (C_m) and conductance (G_m) data.²⁴ ϵ' and ϵ'' are obtained from the capacitance and conductance measured under various illumination intensities, respectively. In Eq. (3), ω and C_m are the angular frequency and the measured conductance values, respectively. The loss tangent ($\tan\delta$) can be expressed as follows²⁵:

$$\tan\delta = \frac{\epsilon''}{\epsilon'} \quad (4)$$

The ac electrical conductivity (σ_{ac}) of the material is given by the following equation²⁰:

$$\sigma_{ac} = \omega C \tan\delta(d/A) = \epsilon''\omega\epsilon_0 \quad (5)$$

Figures 4a–4c show the ϵ' - V , ϵ'' - V , and $\tan\delta$ - V curves for Au/PVA(Co,Ni-doped)/ n -Si Schottky diodes under various illumination intensities at room temperature. As shown in Fig. 4a, the values of ϵ' increase with the increasing illumination level and gate voltage. The ϵ' - V characteristic has an anomalous peak at about 1.1 V. In the absence of an electric field, the charge carriers that bind to different localized states would show different dipole orientations. An electron can hop between a pair of these centers under the effect of an ac field, leading to the reorientation of an electric dipole. This process would cause an increase to a change in the dielectric constant values. Hence, the increase in the dielectric constant with the increasing illumination level can be attributed to the dipole effect.

As shown in Figs. 4b and 4c, ϵ'' and $\tan\delta$ increase slightly with the increasing illumination level. At each illumination level and in dark, the ϵ'' and $\tan\delta$ stay nearly constant with the increasing voltage in the range of approximately (-1.5) – (0.5) V, but above 0.5 V, the value of the ϵ'' and $\tan\delta$ show sharp increase with the increasing gate voltage. In fact, ϵ' - V characteristic in Fig. 4a shows an anomalous above 0.5 V. These behaviors depend on a number of parameters such as doping concentration, interface state density, series resistance of diode, and the thickness of the interfacial layer.^{26–28} It is well known that the capacitance and conductance are extremely sensitive to the interface properties and series resistance.²⁹

The illumination intensities dependence of the ϵ' , ϵ'' , and $\tan\delta$ of Au/PVA(Co,Ni-doped)/ n -Si SDs at about 1.1 V is presented in Figs. 5a–5c, respectively. As it can be seen in these figures, the values of ϵ' and ϵ'' increase with the increasing illumination level. Generally, the polarization can be classified in four categories, namely: electronic, ionic or atomic, dipolar or oriental, and interfacial polarization.^{30,31} Also, each polarization mechanism involves a short range motion of the charges and contributes to total polarization of the sample. Among them, the first two mechanisms can occur only in the high frequency range of 10^{10} – 10^{15} Hz. However, dipolar or oriental polarization can occur in intermediate or high frequency range of 1 kHz–1 MHz due to their longer relaxation time, and may originate from the presence of permanent orientable dipoles, impurities, and surface charges. The interfacial polarization is

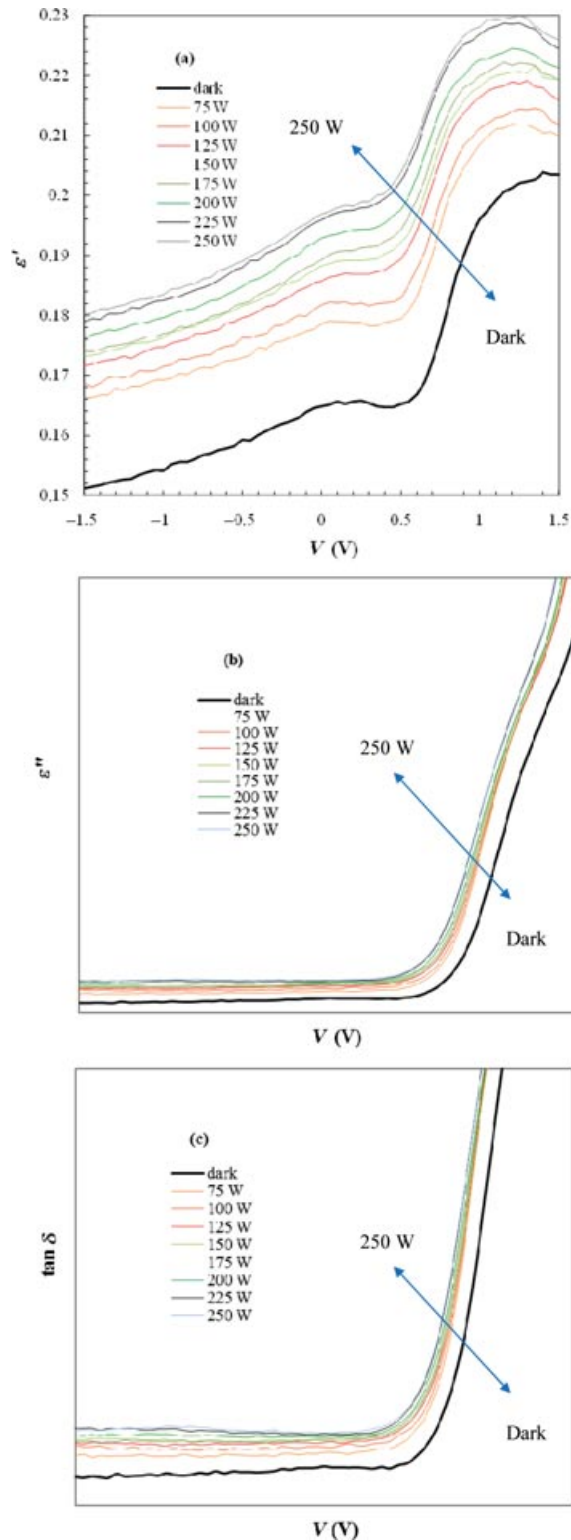


FIGURE 4. Applied voltage dependence of (a) ϵ' , (b) ϵ'' , and (c) $\tan \delta$ for Au/PVA (Co,Ni-doped)/n-Si SD under various illumination intensities at room temperature.

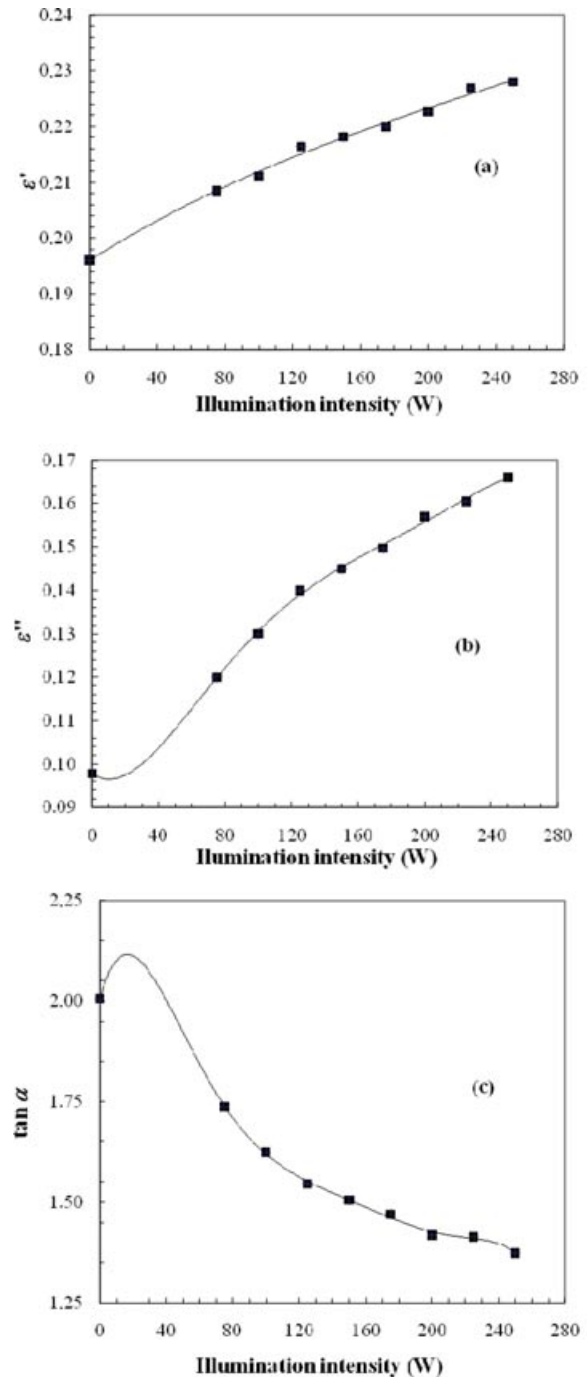


FIGURE 5. Illumination dependence of (a) ϵ' , (b) ϵ'' , and (c) $\tan \delta$ for Au/PVA(Co,Ni-doped)/n-Si SD at room temperature.

more sensitive in low frequencies ($f < 1$ kHz) and may even extend to few kilohertz range, and this mechanism occurs when mobile charge carriers are impeded by a physical barrier that inhibits charge

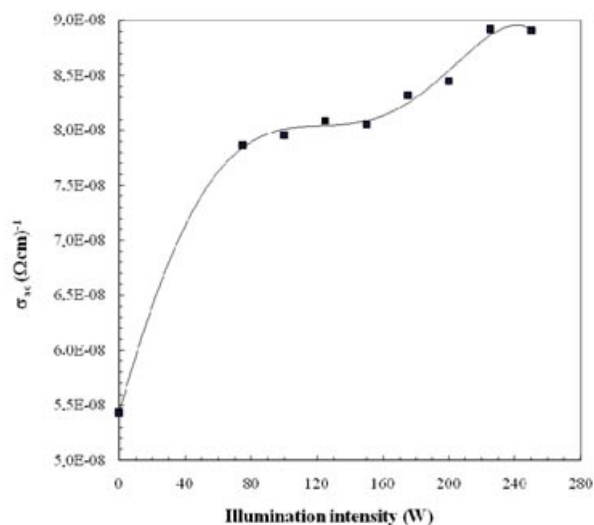


FIGURE 6. Illumination dependence of ac electrical conductivity (σ_{ac}) for Au/PVA(Co,Ni-doped)/*n*-Si SD at room temperature.

migration. Therefore, the last two types of polarization play a main role in our calculations. Moreover, in narrow-band semiconductors, the charge carriers are not free to move but are trapped, causing a polarization. By increasing illumination level, the number of charge carriers increase exponentially and thus charge carriers produce further space charge polarization and, hence, lead to a rapid increase in the dielectric constant ϵ' . Furthermore, the increase in illumination intensities induced an expansion of molecules, which causes an increase in the electronic polarization to some extent and, hence, an increase in the ϵ' and ϵ'' of the dielectric material. In recent years, similar results have been reported in the literature.^{32–35}

The illumination intensities dependent σ_{ac} values of Au/PVA (Co, Ni-doped)/*n*-Si SDs at 1.1 V are presented in Fig. 6. As can be seen from the figure, the values of σ_{ac} increase with the increasing illumination level. Such behavior of σ_{ac} can be attributed to the trap charges which have enough energy to escape from the interface traps located at M/S interface in the Si band gap (E_g) under illumination effect ($h\nu \geq E_g$).

The illumination level dependence of the M' and M'' of Au/PVA(Co,Ni-doped)/*n*-Si SDs at 1.1 V is presented in Figs. 7a and 7b, respectively. As can be seen from these figures, the values of M' and M'' decrease with the increasing illumination level.

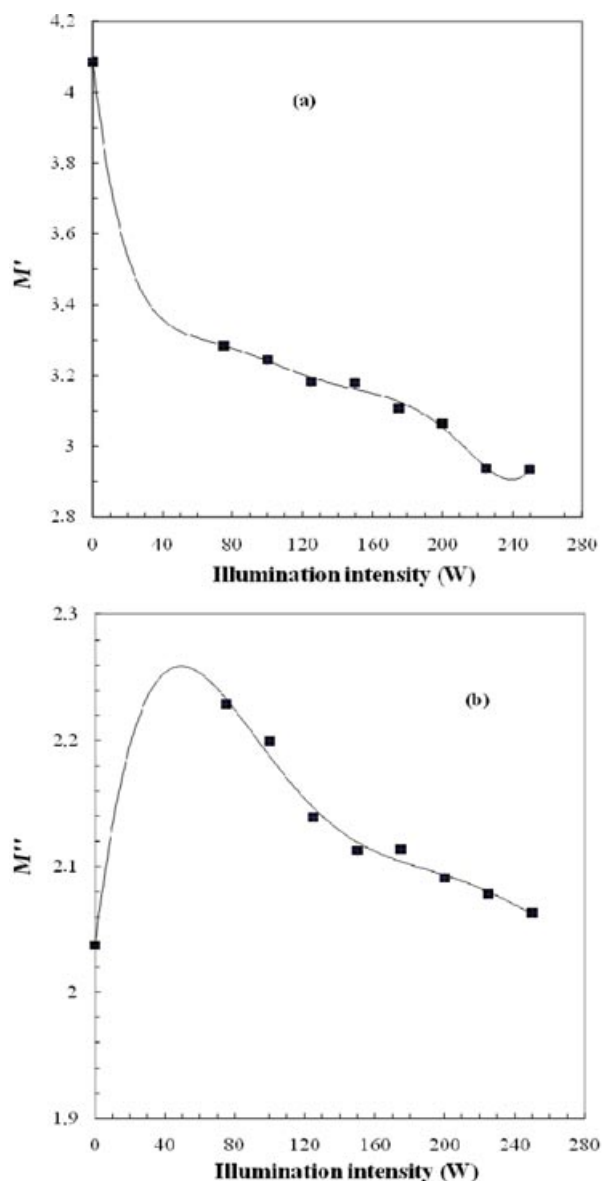


FIGURE 7. Illumination dependence of (a) the real part M' and (b) the imaginary part M'' of electric modulus M^* of Au/PVA(Co,Ni-doped)/*n*-Si SD at room temperature.

Conclusions

The illumination intensity and gate voltage effects on the dielectric properties of Au/PVA (Co,Ni-doped)/*n*-Si SDs have been studied in detail by using admittance spectroscopy method (*C-V* and *G/ω-V*) at room temperature and 1 MHz. The analysis of experimental results has shown that the values of dielectric constant (ϵ'), dielectric loss (ϵ''), loss

tangent ($\tan\delta$), ac electrical conductivity (σ_{ac}), the real part of electric modulus (M'), and the imaginary part of electric modulus (M'') of Au/PVA(Co,Ni-doped)/*n*-Si SDs are dependent on the gate voltages and illumination level. Such behavior of dielectric properties and ac electrical conductivity can be attributed to high mobility of free charges escaped from the traps located between metal and semiconductor, under illumination effect. The change of ϵ' , ϵ'' , and σ_{ac} as a function of gate voltage is a result of restructure and reordering of these trap charges under illumination effect. These results indicate that the Au/PVA (Co,Ni-doped)/*n*-Si SDs can be used as a photodiode and photocapacitive sensor for various visible light applications.

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