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# **Visible Enhanced Photodetector Made by Spray Pyrolysis**

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**Abstract:** Barium–doped TiO<sub>2</sub> / n-Si photodetector was fabricated by spray pyrolysis exhibited visible enhancement responsivity profile with peak response at 600 nm flat response between 650 and 900 nm. The quantum efficiency was 30% and specific detectivity was  $5x10^{12}$  W<sup>-1</sup>Hz<sup>1/2</sup>cm at peak response. The GaAlAs laser diode was used to estimate the rise time of the detector.

# **Introduction**

Titanium dioxide is an n-type semiconducting material with energy band gap of about 3.5 eV [1]. The electron concentration in the conduction band arises primarily from the lack of stoichiometry produced by oxygen deficiency. The high electrical resistivity (about  $10<sup>7</sup>$  Ω.cm [2]) of the undoped TiO<sub>2</sub> films prompted extensive studies on  $TiO<sub>2</sub>$  as a dielectric. Foremost in this regard is the effort reported on  $TiO<sub>2</sub>$  as antireflection coating material in solar cells [3] and as insulating material in capacitor [4]. A high electrical conductivity is not a great challenge and easily can be obtained by doping, for instance with fluorine or barium.

Simultaneously high conductivity and high transparency (i.e., figure of merit parameter is high) put forward  $TiO<sub>2</sub>$  in the list of transparent conductive oxides (TCO). Wide investigation had been focused on TCO semiconductor as photovoltaic devices such as  $SnO<sub>2</sub>/Si$  [5]. ITO/Si [6],  $In_2O_3$ /Si [7], and ITO /InP [8], while mild investigations are found on  $TiO<sub>2</sub>$ /semiconductor photovoltaic devices [9, 10].

In the case of Ba-doped  $T'O<sub>2</sub>/n-Si$ heterojunction, the deposited TCO semiconductor acts as a window for

wavelengths more than 350 nm, while the substrate semiconductor acts as an absorber for the transmitted photons up to 1100 nm (i.e., the cut-off of silicon). When the resistivity of  $TiO<sub>2</sub>$ film is lowered by doping, the series resistance will be low and hence, PV parameters may be reinforced.

This paper is the first reported study on n-TiO<sub>2</sub>:Ba/n-Si isotype heterojunction photodetector fabricated by the low cost spray pyrolysis technique.

### **Experiment**

#### *Spray–Pyrolysis Epitaxy*

TiO2:Ba films were sprayed onto 111 single crystal n-type silicon of 3-5 Ω.cm resistivity. The solution of the spraying was prepared by dissolving 0.479 g metallic titanium and 0.197 g barium carbonate in 100 ml of concentrated HCl acid. After the dissolving, the solution was diluted by adding 100 ml of distilled water. The total solution will contain  $0.1$  M of TiCl<sub>3</sub> and  $0.01$  M of BaCl<sub>2</sub>. The chemical reaction is:

$$
Ti + BaCO3 + 5 HCl
$$
\n
$$
TiCl3 + BaCl2 + OCl2 + H2O + OCl2
$$

 TiCl3 + BaCl<sup>2</sup> + 3H2O TiO<sup>2</sup> + BaO + 5HCl + 1/2H<sup>2</sup>

The silicon substrates were maintained at 400°C during spraying. Thickness obtained was between 20 and 40 nm.

# *Photoresponse Measurements*

After Al ohmic contact, the  $Al-nTiO<sub>2</sub>:Ba$ /nSi-Al photodetectors were illuminated by monochromatic light in the range of 400-1100 nm with the help of monochromator. The rise time was determined by using 200 ns-pulsed GaAlAs laser diode of 10 kHz frequency.

#### **Results and Discussion**

Figure 1 shows typical spectral responsivity plot of n-TiO<sub>2</sub>:Ba /n-Si isotype heterojunction. It is obvious from the figure that there are two distinct regions. The first one is situated at around 600 nm. This peak is probably belonging to titanium oxide. The second region which

starts from 650 nm shows flat response (i.e., responsivity is independent on wavelength) up to 900 nm. This distribution is dissimilar to that of diffused silicon p-n junction. This effect is due to the wide-bandgap of  $TiO<sub>2</sub>$ semiconducting material which resulted in high responsivity at shorter wavelengths (visible enhanced photodetector) i.e., the absorption of high-energy photons occurs in diffusion length of  $TiO<sub>2</sub>$ . It is evident that this photodetector can be used to detect many lasers e.g. He-Ne laser, Ar laser, and GaAlAs laser. The quantum efficiency curve is shown in Fig. 2. At peak response, the quantum efficiency is 30%. This high value of quantum efficiency as compared with other heterojunctions [11] is ascribed to more photon absorption at short wavelengths. Furthermore, the low value of refractive index for  $TiO<sub>2</sub>$  is a reason for increasing internal quantum efficiency. Room temperature specific detectivity is illustrated in Fig. 3. Maximum value  $(5 \times 10^{12} \text{ cm}.Hz^{1/2}.W^{-1})$  was obtained at peak response that indicates high value of shunt resistance and hence, the leakage current will be low.



 **Wavelength (nm)**

Fig. 1 Spectral Responsivity Plot of n-TiO<sub>2</sub>:Ba/n-Si Heterojunction Detector.



The photographic portrait shown in Fig. 4 demonstrates the profile of the output photovoltage respect to time when the detector is irradiated by laser pulses (904 nm). The rise time of photodetector measured from 10% to 90% of the signal was 50ns (taken at  $V_L$ =10 V, R<sub>L</sub>=50 $\Omega$ ). The fall time shows plain delay, which can be attributed to the large lattice mismatch, which produces high density of interface states, so the recombination centers will be high.



**Fig. 4** A Photograph of pulse waveform of photodetector.

# **Conclusions**

Isotype  $n-TiO<sub>2</sub>:Ba$  /Si photodetector introduces more absorption at high energy photons and responsivity profile gives its peak at



**Fig. 2** Quantum efficiency curve. **Fig. 3** Room temperature detectivity vs wavelength.

600 nm. Interface states greatly affect the fall time of the detector.

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تصنيع كاشف يمتلك استجابية عالية في المنطقة المرئية بطريقة الرش الكيمائي الحراري

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يتضمن البحث ، تصنيع كاشف TiO2/n-Si وذلك برش غشاء  $\rm TiO_2$  المشوب بالباريوم على شرائح سليكونية مانحة . أظهرت نتائج االستجابية الطيفية للكاشف أنه يمتلك استجابية عالية في المنطقة المرئية من الطيف وأن قمة االستجابة كانت عند الطول الموجي 011 نانومتر ، وقد لوحظ أن المنطقة الطيفية المحصورة بين001 و911 نانومتر ذات استجابية ثابتة . كانت أعلى قيمة للكفاءة الكمية 01 % . بينما بلغت قيمة الكشفية النوعية **الخالصة**

.  $500\times10\times10\times1$ سم هيرتز  $^{-2}$  واط $^{-1}$  عند الطول الموجي 600 نانومتر جرى حساب زمن النهوض للكاشف بأستخدام ليزر GaAlAs