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Gallium nitride nanoparticles for solar-blind detectors¶

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Abstract. We investigate the properties of GaN semiconducting nanoparticles as a potential candidate for photodetection in the solar-blind region. The photocurrent spectral response is studied spanning the range 1·6–5·5 eV. A significant fraction of the response is in the range 4–5·5 eV. The results are compared to other optical properties and the origins of the features observed in the spectra are speculated upon.

Keywords. GaN; nanoparticles; photodetector; photocurrent.

1. Introduction

Large band-gap materials such as GaN offers interesting properties required for UV photodetection and 'solar blind detectors. Solar blind detectors are required to respond to UV light and be insensitive to the large part of the solar spectrum (> 300 nm). This value of wavelength has been established from the fact that there are few photons in the solar emission with a wavelength shorter than 285 nm which reach the surface of the Earth due to atmospheric absorption. The research work on short-wavelength UV detectors has therefore been recently focused on realizing short-wavelength 'solar-blind' detectors. There have been a growing number of applications that require the use of such sensors, examples of such applications include UV astronomy, flame detection, furnace control, engine monitoring, water purification, UV radiation dosimetry, pollution monitoring, optical autocorrelators used to characterise ultrafast pulse lasers, early missile threat warning, chemical/biological battlefield reagent detectors, and space-to-space communications.[1,2] A novel consumer gadget available in the market presently is the UV sensor built into wristwatches and clip-on watches which monitors the UV content of the sunlight. In many of these applications, it is important to detect UV light without detecting the infrared or visible light, in order to minimize the chances of false detection or high background.

Typical design requirements for these products are: (i) active layer of visible-blind semiconductors, (ii) absence of filters, (iii) photovoltaic mode of operation eliminating the need of an external bias. Several combinations of semiconductors based on Si, Ge, GaAs, SiC have been looked at to realize efficient solid-state UV detection to replace the photomultiplier tubes and extend the spectral window. It is only in the second half of the 1990s that wide bandgap III-nitride semiconductors and, in particular, AlGaN have

¶Dedicated to Professor C N R Rao on his 70th birthday
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emerged as the most promising material systems for such a device. Although the thrust behind most of the research work on III nitride semiconductors and, in particular, AlGaN materials had been the realization of blue light emitting diodes and lasers, the technological advances that resulted have renewed the interest and led to significant progress in UV detectors.[1]

Apart from the advances in wide band gap semiconductors where the fabrication process involves high temperature epitaxial growth techniques, there has been considerable exciting research in the area of nanoparticles of these semiconductors which are processed using low temperature routes. The distinctiveness of the nanoparticle properties arises from the nanoparticle-size dependent fundamental properties such as ionisation potential, melting point, optical fluorescence and absorbance.[3,4] Typical range of size to observe these variation in properties depend upon the solid being periodic over a range in the nanometer regime. In case of nanoparticles of semiconductors such as cadmium sulphide CdS and cadmium selenide CdSe; when the particle size is smaller than that of the exciton in the bulk semiconductor the lowest energy optical transition significantly increases due to quantum confinement.[5] By precisely controlling the size and the surface of a nanocrystal, its properties can be tuned. It was demonstrated that the spectral window for the photoinduced current in the device structures based on these active nanoparticles can be tuned by controlling the particle size. However, due to the large surface to volume ratio, the surface induced defect states, contributing to the sub-gap states was also observed to a significant extent in certain cases. A clear evidence is the decrease in the radiative luminescence with the nanoparticles particle size due to the higher fraction of non-radiative processes mediated by the surface states with increasing size.[6] In this context, GaN nanoparticles offers a good choice with a large intrinsic gap and the availability of routes to synthesize such nanoparticles. It is expected that the presence of shallow traps do not drastically alter the spectral window of operation for designing such photodetectors.

2. Experimental

Gallium nitride nanoparticles were prepared by solvothermal technique. Details of the synthesis and characterization of the GaN particles will be published elsewhere. In a typical solvothermal reaction 0·3 mmole gallium cupferron [$Ga(C_6H_5N_2O_3)_3$] were dissolved in 6 ml toluene. 30 mmole 1,1,1,3,3,3-hexamethyldisilazane [$(CH_3)_3SiNHSi(CH_3)_3$] was added to it. The mixture was transferred in a teflon-lined autoclave (20 ml capacity). The autoclave was maintained at 240°C for 3 h and then allowed to cool to room temperature. The precipitate obtained was then washed with absolute ethanol and then dried at 70°C for 12 h.

Transmission electron microcopy observation revealed that the dried product contains hexagonal GaN particles of average diameter 5 nm. Particles of different sizes were obtained by varying the concentration of Gallium cupferron under the same reaction condition.

Specific precautions were used to perform measurements of the current induced by photoexcitation in the range (200–400 nm). UV enhanced 150 W xenon lamp was used as the light source in conjunction with a UV monochromator. A reflective metallic grating blazed at 300 nm was used for dispersing the light. The transmitivity of the conducting ITO coated on quartz which was used as the substrate was characterized prior to coating with the nanoparticles and used for normalizing the data to obtain the external quantum efficiency of the response. The substrates used had typical transparency of 30% at 250 nm. Conventional lock-in measurements were performed to obtain noise free light-generated signals from the device. For high resistance photoconductors, a constant voltage circuit is preferred and the signal is detected as a change in current in the bias circuit.

Typical device of 2 mm × 2 mm area was fabricated by spin coating and drop casting the GaN dispersion of thickness in the range of 200–300 nm on a pre-patterned ITO substrate. Thermally evaporated Al or Au on the GaN were used as the cathodic contact.

3. Results, discussion and conclusion

The current voltage characteristic of the device is shown in figure 1. The I–V curve is significantly non-linear, with a blocking behaviour at low voltage which gradually opens up and the current increases nonlinearly beyond 2 V. Modelling this I–V obtained at room temperature is quite complex since several mechanisms are involved in determining the dark current–voltage characteristics of the wide gap semiconducting photodiodes. The dark current is the superposition of current contributions from three device regions: bulk, depletion region, and surface. Further distinction is done in terms of the thermally generated current in the bulk and depletion region, surface leakage currents and the space-charge limited current which are necessary to apply model fits. This can be done by assuming a dominant mechanism prevailing in a certain voltage and temperature range, efforts are currently underway in this direction to understand the I–V response in the different ranges.

However, upon photoexcitation a clear asymmetry in the current with respect to the external voltage bias, measured under illumination, is observed as shown in figure 1a, which can be accounted by effects such as a possible schottky formation of semiconducting layer with ITO, and the differences in the charge carrier (*p* and *n*) generation,

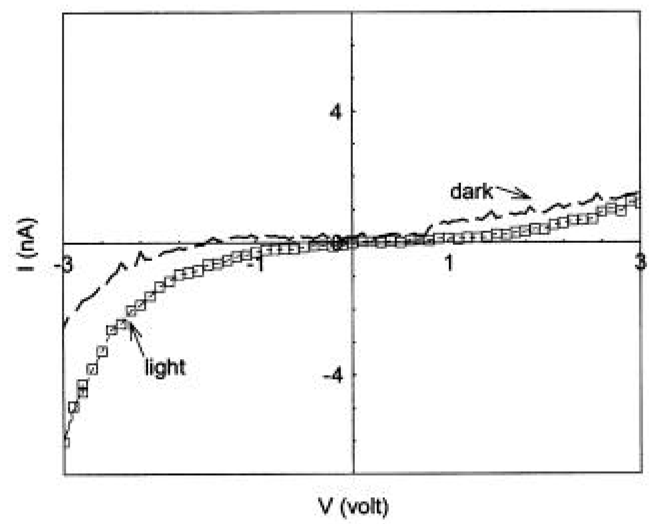

Figure 1. Current–voltage response under dark and illumination conditions (l = 310 nm) of the ITO/GaN/Al device.

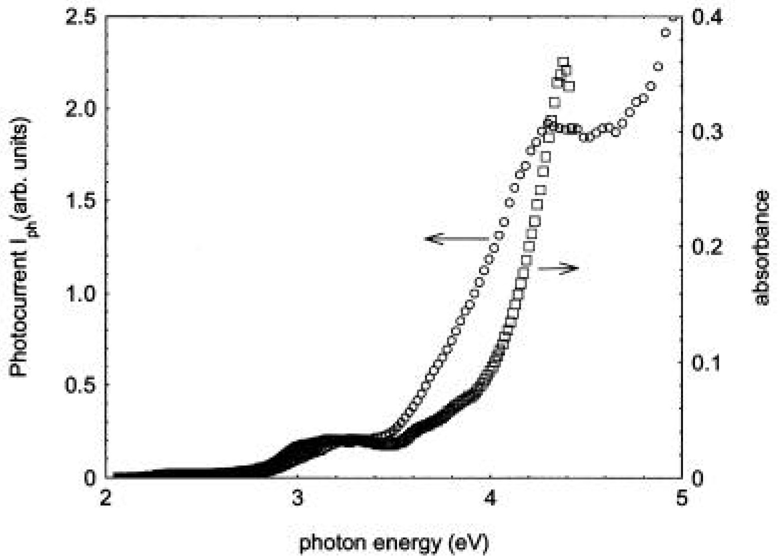

Figure 2. Normalised photocurrent spectral response $I_{ph}(\lambda)$ for the ITO/GaN/Al device and absorbance of the GaN nanoparticle film.

transport and sweep-out rates. The short-circuit current at 0 V was not significant, indicating low built-in field prevailing in the device.

The red-shifted absorption and the luminescence features of these nanoparticles indicate the size dependent electronic structures. The photocurrent spectral response at a reverse voltage bias of 4·5 V along with an absorbance of the GaN nanoparticle is depicted in figure 2. The photocurrent response has distinct features between 3 and 5 eV. The photocurrent was quite insignificant in the measurement range below 3 eV and consists of a small contribution in this region with a local maxima at 2·6 eV and width of 0·2 eV. Bulk GaN has found to be dominated by a radiative trap state giving rise to luminescence at 2·1 eV, and weaker blue emission at 3·4 eV which corresponds to the band edge luminescence.[7] In a first approximation, the photocurrent in presence of an electric field can be thought to be a complementary process to the radiative recombination events. The absence of photocurrent from these trap-states in this spectral region can then be interpreted in terms of a shift of the trap states with decreasing particle size and absence of bulk GaN in the sample.

The $I_{ph}(\lambda)$ closely follows the absorbance indicating that the current is primarily driven by the charge carrier generation processes. In a simplistic sense, the features in $I_{ph}(\lambda)$ can be interpreted to arise from trap or defect states ($3\text{ eV} < E < 3{\cdot}5\text{ eV}$) and band-edge states at $E > 3{\cdot}5$ eV. This interpretation is consistent with the photoluminescence features of the sample. The finite width and the spread of $I_{ph}(\lambda)$ around the band-edge can arise from the dispersity of the particle size, and broadening effects such as urbach tails, shallow impurities and surface strain effects.[8] This interpretation needs to be confirmed and necessitates systematic studies of $I_{ph}(\lambda)$ with size variation of the nanoparticle. Excitonic levels play an important role in the optical properties of GaN.[9] The fundamental near bandgap A, B and C-excitons in GaN are connected with the splitting in the valence band top of GaN into the three states Γ_9, Γ_7, and Γ_7 . It is expected that excitonic features will be clearly manifested at low-temperature (< excitonic binding energy of ~ 15 meV) in the $I_{ph}(\lambda)$ measurements and its dependency on electric field. Upon analysing the derivative spectra of $I_{ph}(\lambda)$, and extrapolating the band-edge region to the energy axis, a higher estimate of the onset for photogenerated charge carrier generation of ≅ 3·8 eV is obtained compared to bulk GaN value of 3·4 eV, pointing out to the size dependent electronic transition in these materials.

From the device point of view, it is interesting to observe from the area under $I_{ph}(\lambda)$ that more than 95% response comes from $\lambda < 400$ nm and about 60% comes from the region $\lambda < 300$ nm; the solar-blind region. It may be possible to improve these spectral properties and responsivity by optimising the size and controlling the defect contributions. In summary, our initial results point to these GaN nanoparticles as promising alternative candidates for solar-blind UV photodetectors.

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