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Electrical and photoresponse properties of Co$_3$O$_4$ nanowires

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Electrical and photocurrent characteristics of single Co$_3$O$_4$ nanowire devices were studied systematically. Current-voltage characteristics’ measurements and impedance spectroscopy of single Co$_3$O$_4$ nanowire devices were performed and analyzed using possible mechanism. Photoresponses of individual nanowires were obtained by global irradiation of laser beams with photon energies above band gap and at sub-band gap of the nanowires. The magnitude of photocurrent and its response time revealed that defect level excitations significantly contribute to the photoresponse of Co$_3$O$_4$ nanowires. In addition, the electrically Ohmic nature of the nanowire/Pt contact and p-type conductivity of Co$_3$O$_4$ nanowire is extracted from the current-voltage characteristics and spatially resolved photocurrent measurements. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4712497]

I. INTRODUCTION

Metal oxide nanostructures have great potential as a low cost and high performance alternative for several optoelectronic applications including photodetectors, sensors, energy storage and lasers, among others. However, the large surface-to-volume ratio induced properties and other unique nanoscale size effects make the design and performance optimization of such nanoscale devices severely complex. One of the key issues of nanodevices is in evaluating and controlling various factors of contact interfaces on their characteristics. The photoconductivity of nanowires for example, depends sensitively on multiple factors such as the work function of the metal contact electrode, design, and gap between the electrodes and also on the device fabrication methodologies. It is also known that the optoelectronic properties of metal oxides nanowires can be tailored by engineering the nanowire/metal interface into either a rectifying or an Ohmic contact. Therefore, it is important to characterize the electrical nature of nanowire/metal contacts using non-destructive methods to obtain better understanding on nanowire optoelectronics. Nanostructures of cobalt oxide (Co$_3$O$_4$) were shown to exhibit enhanced functionalities over its coarse grained structures in several applications including Li ion battery and gas sensing. Bulk Co$_3$O$_4$ is a p-type semiconductor with an indirect band gap of 1.6–2.2 eV and its nanostructures are also anticipated to have potential in optoelectronic applications.

In this paper, we report the electrical and photoconducting properties of individual Co$_3$O$_4$ nanowires. Two terminal current-voltage (I-V) characteristic measurements and impedance spectroscopy of single Co$_3$O$_4$ nanowire devices were performed and analyzed using possible mechanism.

The photoresponse of individual nanowires is studied by two approaches: first by irradiation of laser beam uniformly over the entire nanowire device (global irradiation) and second via selective irradiation of diffraction limited focused laser beam (localized irradiation) on different sections of the nanowire device. Photocurrent and response time measured upon global irradiation of laser sources emitting photons with energies above band gap and at sub-band gap of the nanowire revealed that defect level excitations significantly determine the photoresponse of Co$_3$O$_4$ nanowires. The electrically Ohmic nature of the Co$_3$O$_4$ nanowire/Pt contact and p-type conductivity of the nanowire was extracted from the electrical and spatially resolved photocurrent measurements.

II. EXPERIMENT

Free standing Co$_3$O$_4$ nanowires were synthesized using the previously reported method. Single nanowire devices were fabricated by transferring individual nanowires from the growth substrate to SiO$_2$/Si substrates with photolithographically defined metal (Au(100 nm)/Cr(10 nm)) finger electrodes (of gap ~10 µm). Pt metal contact electrodes were fabricated on both ends of the nanowire using focused ion beam deposition (FIBD, Quanta 200-3D dual beam FIB-SEM, FEI, Ga$^+$ ion beam operated at 30 kV, 50 pA). The electrical measurements were carried out using Keithley 6430 source-measurement unit. For localized photocurrent measurements, continuous wave laser beam from a diode laser (532 nm, SUWTECH, LDC-2500) was focused into a tiny spot (spot size <1 µm) via an objective lens (100×, NA ~0.7) of an optical microscope (Leica DMLM). The Si substrate with test devices was positioned onto the optical microscope sample stage, and the position dependant localized photocurrent was measured by irradiating the focused laser on different sections of the nanowire device.
III. RESULTS AND DISCUSSIONS

A. Single Co$_3$O$_4$ nanowire electrical properties

Top-left inset of Fig. 1(a) shows a SEM image of a typical Co$_3$O$_4$ nanowire device. The thickness of the Pt deposit was $\sim$200 nm. Figure 1(a) shows typical $I$-$V$ curve of Co$_3$O$_4$ nanowire for a continuous voltage sweep of 6 V to $-6$ V, recorded at room temperature under ambient conditions. The Co$_3$O$_4$ nanowire devices exhibited a nonlinear $I$-$V$ characteristic, which was fairly symmetrical to both positive and negative voltage sweeps. For a contact between a high work function metal and low work function p-type semiconductor (work function of Pt, $\Phi_m \sim 5.65$ eV and Co$_3$O$_4$, $\Phi_s \sim 4.3$–4.5 eV (Ref. 14)), the parameter, $\Delta = 1/2E_g - \Phi_m + \Phi_s$ turned out to be negative suggesting an Ohmic contact. Here, $E_g$ is the band gap of the Co$_3$O$_4$ (1.5–2.2 eV). In addition, the $I$-$V$ curve revealed a linear Ohmic response for small voltages and deviation from the linearity occurred gradually as applied voltage increases (as evident from the bottom-right inset of Fig. 1(a)). This implies that the nonlinear characteristic of the two terminal devices is likely to be originated from the intrinsic transport property of the Co$_3$O$_4$ nanowire.

The nonlinear $I$-$V$ characteristic of the high aspect ratio nanowire with Ohmic contacts and low carrier density arises probably as a result of the space charge limited (SCL) electrical transport. Recent studies have established that the current density ($J$) through nanowires in the SCL regime, which is different from that of bulk by a scaling factor, can be expressed as,

$$J = \zeta \frac{dV^2}{L^2},$$

(1)

where $d$ is the radius, $L$ is the length of the nanowire between the electrodes, $\varepsilon$ is the dielectric constant of the nanowire material, and $\mu$ is the mobility of the charge carriers. In the limit of $d/L \ll 1$, the scaling factor $\zeta \sim \zeta_0 (d/L)^{-2}$, with $\zeta_0$ a numerical constant close to unity. As displayed in Fig. 1(b) plot of $I$ versus $V^2$ renders a straight line, which is consistent with the SCL based electrical transport. Since the $I$-$V$ characteristics of Co$_3$O$_4$ nanowires at low voltages show Ohmic response, linear fitting of $I$ versus $V^2$ curve was carried out for moderate voltage range. In addition, above 4 V is excluded from the curve fitting as contributions such as joule

![Graphs and plots](image-url)
heating may affect the $I-V$ characteristics of the nanowire at higher voltages. The mobility of the nanowire in the SCL regime is given by $\mu = \frac{IL}{V^2}$. From the slope of the linear fit of $I$ versus $V^2$ curve and from the dielectric constant of Co$_3$O$_4$ (12.9 (Ref. 18)), the mobility of the nanowire is estimated to be $\sim 1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.

Impedance spectroscopy was performed on individual single crystalline Co$_3$O$_4$ nanowire device, and the measured impedance and phase as a function of the ac modulation frequency are shown in Fig. 1(c), with the negative phase values corresponding to capacitor like behaviour. The absolute capacitances deduced from the impedance ($C = 1/(\omega Z)$, Fig. 1(d)) illustrated the origin of different capacitances in the nanowire. While the capacitance at high frequencies is associated with the geometric capacitance ($C = \varepsilon A/d$), the capacitance at intermediate frequencies originated from the space charge region in the nanowire.\(^1^9\) The capacitances in the low frequency regime correspond to the trapping-detrapping of the charge carriers in the nanowire. If the underlying mechanism is the standard Debye polarization relaxation of the molecules under the applied electric field, the capacitance values at low frequencies are expected to reduce with frequency. On the contrary, capacitance arising from charge trapping phenomena due to interfacial charging or trap-assisted charging would exhibit increase in capacitance as the probing frequency reduces.\(^2^0\) Therefore, the capacitance behaviour of the nanowires at low frequencies shown in Fig. 1(d) is likely to be originating from the trapping-detrapping mechanism of the majority carriers in the nanowire. The capacitance analysis implies that the trap levels contribute to the whole as a specific $RC$ circuit and intriguingly, the contribution due to trapping exceeds the geometric capacitance. The capacitance spectra reaffirm our observations of SCL transport and further support our analysis of estimation of trap limited mobility. The above calculated mobility of Co$_3$O$_4$ nanowires is one order of magnitude higher than that of Co$_3$O$_4$ thin film,\(^1^8\) which can be justified primarily due to its higher crystallinity.

B. Photocurrent measurement using broad beam irradiation

Photoresponse of the single nanowire devices was studied by irradiating lasers of photon energy above ($\sim 2.3 \text{ eV}; 532 \text{ nm}$) and below ($\sim 1.1 \text{ eV}; 1064 \text{ nm}$) the band gap energy of Co$_3$O$_4$. Fig. 2(a) shows the $I-V$ characteristics of a typical nanowire device in dark and upon irradiation of different intensities of 532 nm laser beam. From the $I-V$ curves, it is clear that the symmetric-nonlinear characteristic remains unaltered under laser irradiation. However the slope $dV/dI$
has decreased after irradiation. Notably, the change in slope of \( I-V \) curves depends on the applied bias and becomes more prominent towards higher voltages.

To examine the photoresponse of the nanowire devices, the time evolution of the photocurrent and its decay were studied while the device was biased with a constant voltage (3 V). Upon illumination, the photocurrent increased rather rapidly initially before turning into a more gradual change and finally stabilized to a maximum value over time. As the laser beam was blocked, the current dropped following a similar trend as the rising curve and reached the dark current after a few seconds. For example, Fig. 2(b) shows typical photocurrent-time response (\( I-t \) curve) of the nanowire towards 532 nm laser irradiation (for a fixed laser intensity of \( 16 \pm 3 \, \text{mW/mm}^2 \)). The rise and decay of photocurrent can be expressed in the form of Eqs. (2) and (3), respectively,

\[
I = I_0 + A_1(1 - e^{t_1/t_2}),
\]

\[
I = I_0 + A_2(e^{t_2/t_1}),
\]

where \( I_0 \) is the dark current, \( t_0 \) is the initial time, \( A_1 \) and \( A_2 \) are the amplitude of photocurrent, and \( t_1 \) and \( t_2 \) are the response time of the rise and decay curves, respectively. By fitting the photocurrent rise and decay curve using Eqs. (2) and (3), the average response time \( t_1 \) and \( t_2 \) are estimated to be approximately 13.7 and 11.3 s, respectively (Fig. 3(c)).

Besides the indirect band gap of the Co\(_3\)O\(_4\), the charge trapping surface defect states inherent to nanoscale structures may cause the observed slow photocurrent response time.

To elucidate the effects of photon energy, the \( I-V \) and \( I-t \) curves were recorded upon global irradiation of 1064 nm laser of sub-band gap energy on the Co\(_3\)O\(_4\) nanowires (Figs. 2(d)–2(f)). The \( I-V \) characteristics and \( I-t \) response upon 1064 nm laser irradiation revealed that sub-band gap illumination generated significant photocurrent in the nanowire. Naturally, the magnitude of the photocurrent was smaller than those generated by laser beam with higher energy (above band gap energy) and approximately the same illumination intensity. The rise and decay curves correspond to the 1064 nm laser irradiation were also found to fit reasonably well with Eqs. (2) and (3), and average response time \( t_1 \) and \( t_2 \) were extracted as 12.3 and 11.9 s, respectively.

It is noteworthy that the magnitude of photocurrent and its time responses for above band gap and sub-band gap excitations are comparable. This suggests that the photocurrent characteristics of Co\(_3\)O\(_4\) nanowires are contributed by the excitation of various sub-band gap energy defect levels.23 The band-to-band excitation upon above band gap excitation renders slightly larger photocurrent when compared to the below band gap excitation. However, the defect level excitation with a slow photoresponse naturally determine the response time. In addition, the slow decay responses indicate that the presence of trap centres such as surface states prolongs the photogenerated carrier life time.24

C. Photocurrent measurements by localized laser irradiation

Recently, the spatially resolved photocurrent measurements have emerged as a non-destructive technique to probe and characterize optoelectronic properties of nanodevices and also to determine the effect of metal contacts on the functionalities of such devices.25–29 The spatially resolved and localized photocurrent measurements on Co\(_3\)O\(_4\) nanowire devices were conducted both at zero bias and with constant voltage bias conditions. Fig. 3(a) shows optical micrographs of a nanowire device captured during the photocurrent measurements with the focused laser beam (532 nm) irradiated at different positions along the device. At zero bias, photocurrents of opposite polarity were generated upon irradiation of focused laser beam near the two nanowire/Pt contacts as displayed in Fig. 3(b). However, negligible photocurrent was produced while the nanowire is irradiated near its midpoint. The observed zero bias photocurrent could be due to a photovoltaic effect which arises primarily due to the difference in the mobilities of electrons and holes in Co\(_3\)O\(_4\). Since Co\(_3\)O\(_4\) is a p-type semiconductor, the hole mobility will be much higher than that of electrons. The higher hole mobility eased the diffusion of photogenerated holes from the irradiated nanowire/metal contact through the nanowire. The polarity of the measured photocurrent on either contacts at zero bias support such a scenario of hole diffusion. In addition, the focused laser inducing localized heating and resulting photothermoelectric effect also may contribute the zero bias photocurrent.30,31 Near the midpoint of the
nanowire, the photogenerated carriers are diffused randomly rendering a nearly zero net photocurrent.

To study the effect of applied bias, $I$-$V$ curves were recorded upon the focused laser beam irradiated on different position of the nanowire device as shown in Fig. 4(a). The nonlinear $I$-$V$ characteristic is retained upon localized irradiation of the focused laser beam on different portions of the nanowire. As in global laser irradiation, the resistance of the nanowire has decreased upon localized laser irradiation. The laser irradiation induced drop in resistance significantly increased with applied bias. Furthermore, the drop in resistance upon laser irradiation on contact 1 (biased) and contact 2 (grounded) was much significant than that at the midpoint of the nanowire. The higher photoresponse near the contact could be a result of efficient separation of photogenerated charge carriers at the contacts.

Fig. 4(b) shows that the rising and decaying photocurrent characteristics correspond to periodic irradiation of focused laser beam (532 nm; 1 mW; at a fixed bias of 1 V) at different portions of the nanowire device. Different from the zero bias case, the laser irradiation near the midpoint of the nanowire produced significant photocurrent at a fixed bias of 1 V. Since there is no external driving force at zero bias, the photo-generated carriers near the midpoint of the nanowire diffuse randomly rendering a net zero current. Whereas at a fixed bias of 1 V, the photogenerated carriers are drifted by the external electric field, and a corresponding photocurrent is recorded in the ammeter. Compared to the slow photosresponse upon global irradiation, localized irradiation resulted in a fast rising and decaying photocurrent from the Co$_3$O$_4$ nanowire. The response time in the localized irradiation is shorter than the temporal resolution of the source meter used in our measurements. The striking difference in photocurrent response time upon global and localized irradiation could be a result of the difference in the intensity of the laser beam. The intensity of the focused laser beam ($\sim 10^4$ mW/mm$^2$) is much higher than the broad beam laser ($\sim 10^1$ mW/mm$^2$) and the localized irradiation, and this could result in a fast photoresponse.

IV. SUMMARY

$I$-$V$ characteristics and impedance of single Co$_3$O$_4$ nanowires contacted with Pt metal electrodes were measured and analysed using possible mechanism. The photocurrent and its response time measured upon global illumination of above and sub-band gap energy laser beams revealed that the defect level excitations largely responsible for the carrier photogeneration and transport in Co$_3$O$_4$ nanowires. In addition, the polarity of the photocurrent upon localized irradiation verified the p-type conductivity of the Co$_3$O$_4$ nanowires. The higher photocurrent near the contact can be explained on the basis of efficient separation of photogenerated charge carrier at the contacts.

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