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Electro-physical characterization of individual and arrays of ZnO nanowires

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Capacitance measurements were made on an array of parallel ZnO nanowires embedded in a polymer matrix and provided with two electrodes perpendicular to the nanowires. The capacitance monotonically increased, and saturated at large negative (depleting) and large positive (accumulating) voltages. A qualitative explanation for this behavior is presented, taking into account specific features of quasi-one-dimensional screening. The increasing or decreasing character of the capacitance-voltage characteristics were determined by the conductivity type of the nanowires, which in our case was n-type. A dispersion of the experimental capacitance was observed over the entire frequency range of 1 kHz to 5 MHz. This phenomenon is explained by the slow discharge of the nanowires through the thin dielectric layer that separates them from the top electrode. Separate measurements on individual identical nanowires in a field effect transistor configuration yielded an electron concentration and mobility of approximately $10^{17}$ cm$^{-3}$ and 150 cm$^2$/Vs, respectively, at room temperature. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4926793]

I. INTRODUCTION

Semiconductor nanowires (NWs) have been extensively investigated over the last decades as possible building blocks for new types of nanoelectronic devices. Among the various materials proposed for such structures, ZnO, with its relatively simple growth technology and well-studied band structure has attracted much attention, especially for optoelectronics. On account of the wide band gap of 3.37 eV and large exciton binding energy of 60 meV (or larger due to size quantization), ZnO NWs are promising for photonic applications in the ultraviolet or blue spectral range, and for excitonic solar cells. They may also have several other possible applications such as thermoelectric devices, piezoelectric nanogenerators, photocatalytic cells, optical waveguides, surface acoustic wave devices, mechanical nanogenerators, transparent conductive oxides, as well as chemical and gas sensors.

Besides single NWs, NW arrays are also of great theoretical and practical interest. Such structures do not only compensate the weak output of individual NWs but may exhibit specific properties caused by electric and/or optical interaction between the NWs. Periodic NW arrays with typical interwire distances comparable to the inter-band light wavelength in ZnO may also have some additional functional opportunities that exploit photonic bandgap effects.

Development of NWs and their arrays as nanoscale electronic devices requires determination of basic NW parameters, such as concentration, mobility, and lifetime of carriers. These intrinsic parameters determine the characteristics of field effect transistors (FETs), solar cells and other NW-based devices. In NWs, these parameters may differ from those in bulk samples due to additional carrier scattering, capture, and recombination at the NW surface. There is a need to develop simple and reliable characterization methods to study the intrinsic properties of NWs through measurements on single NWs and on NW arrays. Despite years of research on NWs and studies of possible device applications, challenges exist in their characterization, especially on multi-NW structures (arrays). These challenges exist because standard approaches used for bulk samples are not always applicable. On the one hand, Hall measurements on single thin NWs are very difficult and require sophisticated technology for making lateral contacts. This is a severe impediment to the development of such NWs as FETs and other similar devices. It is therefore important that alternate techniques be developed for measuring carrier concentration and mobility. Moreover, both Hall effect and FET measurements can only be performed on individual NWs. To investigate NW arrays and, in particular, study the above-mentioned effects caused by inter-wire interactions, one should develop some alternative techniques. One such possibility would be capacitance measurements on metal-insulator-semiconductor (MIS) structures that can be analyzed for determination of fundamental NW parameters. This measurement cannot be used for investigations of individual NWs (since the capacity of a NW is very small as compared to that of the external electrodes) but can be applied to NW arrays. Such measurements have been reported on vertical arrays of Si (Ref. 23) and InAs (Refs. 24 and 25) NWs. The NWs in these cases were coated with a thin dielectric layer, followed by metallization to create a metal-oxide-semiconductor capacitor.

In this work capacitance measurements were performed on an array of ZnO NWs fabricated by the vapor-liquid-solid (VLS) technology. The capacitance measurement reported in this work is a very simple strategy for measuring capacitance of the entire array, and does not require special individual
treatment of each NW. Measurements on the NW array were complemented with transport measurement on identical single NWs for determining their basic parameters, such as concentration and carrier mobility.

II. EXPERIMENTAL DETAILS

The ZnO NW arrays used in this experiment were grown on a highly doped $p^+$ Si substrate (resistivity of 0.001–0.005 & ohm; cm) by the VLS growth mechanism, using ZnO nanocrystals as the metal seed to initiate NW growth. The Si substrates were first coated with zinc acetate, which was subsequently decomposed at about 600 K to provide nucleation sites for vertical ZnO NW growth. Synthesis involved heating a source of pure Zn (Alfa Aesar, 99.99% purity) to 700 °C, in flowing gases of oxygen and argon. The seeded substrates were placed in a high temperature furnace, at the downstream end of the growth tube. The growth temperature was about 550 °C, facilitating NW growth but not high enough to cause additional oxidation of the Si substrate. A scanning electron microscope (SEM) image of the as-grown NW array is shown in Fig. 1(a). The length of the NWs in the array was about 2 μm, the diameter was ≈100 nm, and their areal density (estimated by SEM) was about 20 wires/μm². The NWs have a vertical orientation desirable for use in creating the ordered, sandwiched structure required for this experiment. High resolution transmission electron microscope (HRTEM) image of a single ZnO NW shows that it is a perfect crystal with a lattice constant of 0.52 nm along the c-axis (Fig. 1(b)). The high crystalline quality of the ZnO NWs was also confirmed by X-ray diffraction (XRD) studies using Rigaku Ultima III. Fig. 2 shows the XRD spectrum obtained from the as-grown ZnO NW array. The diffraction peaks in Fig. 2 are indexed to the hexagonal ZnO wurtzite structure. The strong (002) peak at $2\theta = 34.36^\circ$ corresponds to the c-axis of ZnO, which relates to the growth direction of ZnO. No diffraction peaks from metallic Zn or other phases were observed in the spectrum. The measured lattice parameter of $c = 0.521$ nm is consistent with Fig. 1(b) and with the lattice constant values reported for bulk crystals of ZnO along the (0001) growth direction.

Following growth, a thin layer of poly-methyl-methacrylate (PMMA) was spin coated on the sample at 2000 rpm for 30 s. The PMMA fills the voids between the NWs, mechanically stabilizes, and electrically isolates them. Two such samples were prepared: in the first case (sample A) the viscosity of the PMMA and its spin coating were controlled to ensure that the NW tips were exposed and can be electrically contacted. In the second case (sample B), a thin layer of PMMA covered the NWs completely. A schematic of the two devices is shown in the inset of Fig. 3. Following spin coating, a layer of aluminum was thermally evaporated to function as the top electrode. The bottom electrode is the heavily doped substrate. Device A (Fig. 3(a)) is thus an array of ZnO NWs contacted at both ends by electrodes, whereas device B (Fig. 3(b)) represents a structure with a thin (not exceeding 200 nm) dielectric PMMA layer between the top electrode and the NWs.

Electrical transport measurements were also performed on single ZnO NWs. The NWs in this case were grown under identical technological conditions but for a longer time, which provided NW lengths exceeding 20 μm. The as-grown NWs were dispersed in alcohol and subsequently dropped on
a $p^+$ Si substrate covered with a 400 nm thick SiO$_2$ layer. Using a mask, two contact pads 20 $\mu$m apart were established at the NW ends, followed by evaporation of Al contacts. To modulate the carrier concentration, the NWs were used in a FET-type configuration, with the highly doped $p^+$ Si substrate serving as the back gate. Transport measurements were performed using a semiconductor parameter analyzer (Agilent Technologies B1500A). For temperature dependent transport measurements, the samples were placed in a temperature controlled (Lakeshore 330) Janis cryostat, where the temperature was varied from 100 to 300 K. An Agilent B1500A semiconductor parameter analyzer in conjunction with an array of ZnO NWs (device B), with their I-V characteristics shown in Fig. 3(b). These measurements were performed on an individual ZnO NW. The results of measurements are presented in Fig. 4(a). The minimal value of current at $V_{gs} = V_T \simeq -3.4$ V corresponds to the complete depletion of the NW. Negative value of $V_T$ indicates that the main carriers in the NW are electrons. Their equilibrium concentration $n_0$ was found using the equation: $n_0 = C|V_T|/(e\pi R^2L)$ with the gate capacitance $C$ given by the equation

$$C = \frac{2\pi\varepsilon_0\varepsilon_{ref}}{\cosh^{-1}\left(\frac{L}{R} + \frac{L}{R}\right)}.$$  (1)

III. RESULTS OF MEASUREMENTS

Comparative I-V measurements on the A and B samples of NW arrays (Fig. 3) show that sample B is characterized by a nonlinear and very high (3 orders of magnitude larger than that of the sample A) resistance. This confirmed the presence of the thin continuous PMMA layer above the NW tips, and in the subsequent capacitance measurements, sample B with its small active conductance was used exclusively.

To determine the type, concentration, and mobility of carriers in the ZnO NWs, three-terminal measurements were performed on a single NW. The results of measurements are presented in Fig. 4(a). The minimal value of current at $V_{gs} = V_T \simeq -3.4$ V corresponds to the complete depletion of the NW. Negative value of $V_T$ indicates that the main carriers in the NW are electrons. Their equilibrium concentration $n_0$ was found using the equation: $n_0 = C|V_T|/(e\pi R^2L)$ with the gate capacitance $C$ given by the equation

$$C = \frac{2\pi\varepsilon_0\varepsilon_{ref}}{\cosh^{-1}\left(\frac{L}{R} + \frac{L}{R}\right)}.$$  (1)

Here, $\varepsilon_{ref} \approx 3.9$ is the effective dielectric constant for the SiO$_2$ back-gate dielectric with the thickness $t_{ox}$, $R$ is the NW radius, and $L$ is the distance between the source and drain contacts. At the room temperature the carrier concentration in the ZnO NW is estimated to be $n_0 \approx 1.3 \times 10^{17}$ cm$^{-3}$. Applicability of the formula Eq. (1), used by many authors conducting similar measurements, requires, in fact, some justification. It is derived for a metallic cylinder above a conducting plate and hence is valid if the potential variations throughout the NW cross-section can be neglected. Estimates show that this corresponds to the condition $t_{ox} \gg \min\{r_s, R\}$, where $r_s$ is the screening radius in the NW material. In our case, for the estimated $n_0$, at room temperature, $r_s \approx 100$ nm, $R \approx 50$ nm, $t_{ox} \approx 400$ nm; thus Eq. (1) is appropriate for our analysis.

From the linear part of the $I_{ds}$ vs $V_{gs}$ dependence shown in Fig. 4(a), the field effect mobility $\mu_{FE} = \frac{d^2}{dV_{ds}dV_{gs}}$ was found to be approximately $150$ cm$^2$/V$\cdot$s$^{-1}$. This value is comparable to the results reported for other ZnO nanostructures–thin films and nanoplates. It also compares favorably with electron Hall mobility of about $200$ cm$^2$/V$\cdot$s$^{-1}$ reported for bulk ZnO single crystals.

In order to gain further insights into the conduction mechanism in the ZnO NWs, temperature-dependent I-V measurements were performed on a single ZnO NW contacted by source and drain electrodes. The results are shown in Fig. 4(b); the linear dependence confirms the ohmic character of the contacts. A study of the variation of conductivity with temperature (Fig. 4(c)) shows that below $T = 200$ K, the NW conductivity $\sigma$ has a thermally activated character $\sigma \sim \exp(-E_a/kT)$ with an activation energy $E_a \approx 25$ meV. This is the well known energy level in ZnO related to Zn$_i$ defects.

Since electron transport in a single ZnO NW showed promising results, efforts were then directed towards studying an array of ZnO NWs (device B), with their I-V characteristics shown in Fig. 3(b). These measurements were followed by capacitance measurements on the array. The upper curve in Fig. 5 shows the C-V measurements made on device B at a frequency of 1 kHz with the bias voltage...
varying from $-8 \text{ V}$ to $+8 \text{ V}$. The capacitance was found to saturate at negative voltages to about $150 \text{ pF}$, then increase sharply across $\approx 0 \text{ V}$ and finally tends to saturation again at positive bias greater than $\approx 7 \text{ V}$. The important characteristic of all C-V curves is their frequency dispersion, observed in the whole frequency range covering more than three orders of magnitude. Fig. 6 demonstrates this spectral dependence for positive and negative voltages. In both cases it has a relatively weak character, close to that of a logarithmic function. For comparison, this function is shown by the dashed line in Fig. 6. At positive voltages capacitance dispersion is more noticeable, thus reducing the voltage dependence of capacitance at higher frequencies (Fig. 5).

### IV. DISCUSSION

To give a theoretical description of the C-V characteristic of our structures (device B), we consider a NW in the array, provided with an ohmic contact at $x = 0$ and at its opposite end, $x = L$. A thin dielectric layer separates the top contact from the tip of the NW (schematic shown in the inset of Fig. 3). The equilibrium linear density of electrons in the NW is $n_0$. The voltage $V$ applied to the top contact adds (for $V > 0$) or removes (for $V < 0$) electrons in the NW with the density $\Delta n(x)$, disturbing the initially uniform inter-contact electric field with the potential $\Phi_0 = V x / L$. Effects of screening by quasi-one-dimensional electrons confined in a NW were theoretically considered previously. It was shown

**FIG. 4.** Electrical measurements on a single ZnO NW: (a) dependence of current on the gate voltage; (b) current-voltage characteristics at different temperatures; (c) temperature dependence of conductivity in linear and semi-logarithmic scale.

**FIG. 5.** Capacitance-voltage characteristics at frequencies 1 kHz (1), 2 kHz (2), 5 kHz (3), 10 kHz (4), 50 kHz (5), 100 kHz (6), 500 kHz (7), 1 MHz (8), 2 MHz (9), 5 MHz (10).

**FIG. 6.** Frequency dependence of the capacitance for positive and negative voltages. The dashed curve corresponds to the function $C \sim 1 / \log(f)$. 

that in thin NWs, with the radius $R$ less than both the screening length in bulk material and the characteristic length $l$ of the potential variation along the NW, the potential $\phi$ created by the linear charge $-\varepsilon \Delta n$ inside the NW depends only on $x$ and, with logarithmic accuracy is proportional to the local value of $\Delta n$: $\phi(x) \approx -(e/2\pi \varepsilon_0 \varepsilon_{\text{eff}}) \ln(l/a) \Delta n(x)$, where $\varepsilon_{\text{eff}}$ is the dielectric constant of NW environment. The total potential acting on the electrons

$$\phi(x) = \Phi_0(x) + \phi_s(x) = \Phi_0(x) - \frac{e}{2\pi \varepsilon_0 \varepsilon_{\text{eff}}} \ln \left(\frac{l}{a}\right) \Delta n(x).$$

(2)

The role of $l$ in our case is played by the NW length, which in our structures differs from the intercontact distance $L$ by less than 10%.

In the absence of a current, the relationship between the local values of potential $\phi(x)$ and concentration $\Delta n(x)$ are given by the equilibrium Boltzmann distribution:

$$n_0 + \Delta n(x) = n_0 \exp \left(\frac{\phi(x)}{kT}\right).$$

Substituting this into Eq. (2), we get the equation for $\Delta n(x)$

$$\frac{kT}{e} \ln \left(1 + \frac{\Delta n(x)}{n_0}\right) = \Phi_0(x) - \frac{e}{2\pi \varepsilon_0 \varepsilon_{\text{eff}}} \ln \left(\frac{l}{a}\right) \Delta n(x).$$

(3)

Formula Eq. (3) allows us to make some qualitative predictions. Differentiating it by $\Phi_0$, we get

$$\frac{d(\Delta n)}{d\Phi} = \frac{e(n_0 + \Delta n)}{kT + \frac{e^2}{2\pi \varepsilon_0 \varepsilon_{\text{eff}}} \ln \left(\frac{l}{a}\right) (n_0 + \Delta n)}.$$

Since $\Phi_0$ is proportional to the applied voltage $V$ and $\Delta n$ increases with $V$, we see that the local value of $\frac{d(\Delta n)}{d\Phi}$ at any $x$ is an increasing function of $V$, tending to zero at large negative $V$, when $n_0 + \Delta n \to 0$, and saturating to $\frac{d(\Delta n)}{d\Phi} \to 2\pi \varepsilon_0 \varepsilon_{\text{eff}} \left[\ln \left(\frac{l}{a}\right)\right]^{-1}$ at large positive $V$. The NW capacity is $C = \frac{dQ}{dV}$, where $Q = \int_0^{L} \Delta n(x) dx$ is the total voltage-generated charge in the NW. Hence, the theoretical C-V characteristic should reproduce the behaviour of $\frac{d(\Delta n)}{d\Phi}$, which, in turn, is characterized by the monotonic growth of $C$ vs $V$ and the tendency to saturation at large positive voltages.

The positive sign of $dC/dV$ indicates that $V > 0$ corresponds to an accumulation of carriers in NWs, which confirms the results that the carriers are electrons. This means that the qualitative character of C-V characteristics, even in the absence of any other preliminary measurements allows one to determine the type of NW conductivity. As seen in Fig. 5, there is a tendency of C-V curves to saturate at large negative voltages. Though this tendency is predicted by Eq. (4), the approach becomes inadequate at large negative voltages when the length of the complete depletion layer $l$ in the upper part of the NW exceeds the separation $d$ between the NWs, so that their electrostatic influence can no longer be ignored. It has been shown that at $l \gg d$ the discreteness of NWs becomes of a minor importance and their array can be considered as a bulk semiconductor with the effective concentration $n_{\text{eff}} = n_0 \pi R^2 d^2 \approx 2 \times 10^{16}$ cm$^{-3}$. Nevertheless, due to the increase of the depletion layer with $|V|$, the capacitance will continue to drop at large negative voltage and saturate at a value determined by the contacts when all NWs become depleted, in agreement with the experimental results.

The observed frequency dispersion of the capacitance (Fig. 5) even at rather low frequencies, requires a separate discussion. Similar effects, observed for example, in porous Si, might be typical for low-dimensional systems, and could be attributed to the strong suppression of screening effects in such systems caused by carrier confinement. As a result, the electric field penetrates into the sample at the macroscopic distance $l_E$ and the characteristic time of this field re-distribution is the diffusion time $\tau = R C / D$, which in long NWs may reach rather large values. The diffusion coefficient, $D$, for the mobility value determined above is $4$ cm$^2$/s. However, in our structures with relatively short NWs ($L \approx 2 \mu m$), the maximum possible diffusion time is restricted by the value $L^2/D \approx 10^{-7}$ s and cannot be responsible for the frequency dispersion in the kHz range. On the other hand, the system capacity $C = 100$–200 pF (Fig. 5) and resistance $R \approx 20$ MOhm (Fig. 3(b)) provides a time constant $\tau = RC$ of several milliseconds corresponding to the frequencies 0.1–1 kHz. Since the system resistance is due exclusively to resistance of the thin PMMA layer covering the NW tips (compare Figs. 3(a) and 3(b)), physically these non-stationary effects are caused by the NWs slowly discharging through this layer. For positive (accumulating) voltages the capacitance and hence $\tau$ increase and the frequency dispersion becomes more noticeable.

V. CONCLUSION

In this paper, we demonstrate a relatively simple technique for capacitance measurements on arrays of parallel ZnO NWs grown by the VLS technology. Preliminary measurements on identical individual NWs showed that they are $n$-type with an electron concentration $n_0 \approx 1.3 \times 10^{11}$ cm$^{-3}$ and mobility $\approx 150$ cm$^2$V$^{-1}$s$^{-1}$. The NWs were embedded in polymer and contacted by metal (ohmic) contacts. For capacitance measurements, the top contact was separated from the NW tips by a thin polymer layer. The capacitance increased with the applied voltage, which confirms independently $n$-type conductivity of NWs. The frequency dispersion of capacitance was observed in the whole range 1 kHz–5 MHz used in the experiment. Estimates show that this low-frequency dispersion cannot be attributed to carrier diffusion through the system and is rather explained by the slow discharge of NWs through the thin dielectric.
