Self-attraction among aligned Au/ZnO nanorods under electron beam

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Self-attraction among vertical aligned Au/ZnO nanorods under the illumination of an electron beam has been observed. This phenomenon is attributed to the interaction between the accumulation charges near the metal-semiconductor junctions for two nanorods of different length. A model calculation is presented to explain the observed phenomenon. *© 2005 American Institute of Physics*. [DOI: 10.1063/1.1847713]

The synthesis and wide range of characteristics exhibited by quasi-one-dimensional (1D) nanostructure is one of the most active research fields in nanotechnology and potential applications of 1D nanomaterials have been demonstrated in several areas;[1] with the most current interest being in the manipulation of 1D nanostructures for fabricating nanodevices for sensing,[2] field emission,[3] and optoelectronics.[4] As one of the most important direct band gap semiconductors, ZnO has recently attracted high interest for synthesizing various nanostructures and fabricating nanodevices.[5] One of the techniques being investigated for the growth ZnO nanorod arrays is to use gold as catalyst particles.[6,7] In this technique, Au acts as the nucleation site and is carried on the tip of the ZnO nanorod such that a natural metal–semiconductor junction (MS)[8] is formed. In this letter, we demonstrate an interesting phenomenon of self-attraction among the aligned MS junction arrays under an electron beam in a scanning electron microscope (SEM). A model is presented for interpreting the observed phenomenon.

The aligned ZnO nanorods were grown by the vapor–liquid–solid (VLS) process. A 1 cm by 1 cm *a*-plane orientated sapphire substrate was used for ZnO nanorod deposition. A 4- to 5-nm thick, hexagonal gold catalyst pattern was sputtered onto the substrate using an ordered monolayer array of submicron polystyrene spheres as a mask.[7] Equal amounts (by weight) of ZnO powder and carbon black were mixed in an alumina boat and then loaded at the center of an alumina tube. Ar was used as a carrying gas at a flow rate of 20 sccm. The sapphire substrate was located 12–15 cm downstream from the source materials in a horizontal tube furnace that could be heated to 900 °C at a rate of 50 °C/min. After holding at temperature for 15 min, the furnace was slowly cooled to room temperature.

The as-synthesized ZnO nanorods were first observed using a LEO 1530 field emission scanning electron microscope (SEM) operated at 3 kV. Figure 1(a) is a typical SEM picture showing the hexagonal patterned and aligned ZnO nanorods. The nanorods exhibit an average diameter of ~20 nm and length ranging from 300 nm to 1 μm. The distribution of the nanorods follows the prefabricated pattern, but they grow from a continuous ZnO crystal layer at the bottom. An interesting phenomenon is that, after a short period of observation, some of the nanorods start to bend and make contact with each other. In all of these cases, the gold tip of one nanorod bends to be in contact with the body of another. Usually both nanorods have slightly different lengths. The SEM images shown in Figs. 1(b) and 1(c), which were taken at a tilting angle of 30°, clearly show this process. Comparing the three circled regions shows that all of the ZnO nanorods are straight and vertical at the beginning [Fig. 1(b)]. However, after 30 s illumination by the electron beam, some of the tips of the nanorods suddenly bundled together, as shown in the final picture, Fig. 1(c). Specifically, as shown in the circled regions in Figs. 1(d) and 1(e), one nanorod bends and makes contact with two nanorods on its left after 1 min electron beam illumination.

The configuration of the bunched nanorods is very stable. Figure 2(a) shows the initial contact of four ZnO nanorods. When taken out of the SEM chamber and reexamined after 7 days in air [Figs. 2(b) and 2(c)], the configuration was preserved as shown in Fig. 2(a). The largest distance between the bunched nanorods is ~150 nm.

In order to explain this phenomenon, the crystallography of the ZnO nanorods was first studied using a Hitachi HF 2000 transmission electron microscope (TEM). Figure 3(a) shows a TEM image of a typical ZnO nanorod with a gold nanoparticle at its tip, which acts as the catalyst during VLS

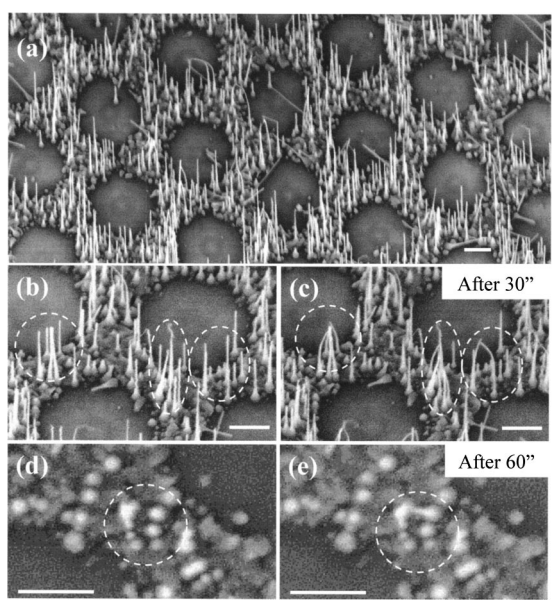

FIG. 1. (a) A low-magnification SEM image of aligned ZnO nanorods; (b), (c) 30° side view of self-attraction phenomenon; (d), (e) top view of self-attraction phenomenon. The scale bars represent 300 nm.

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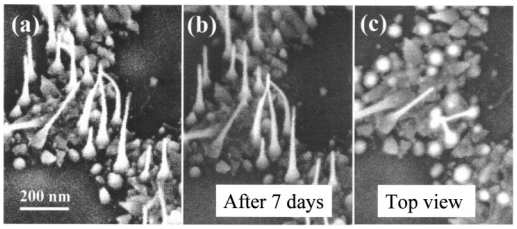

FIG. 2. The ZnO nanorods contacting situation remains after days.

growth. The thickness of the nanorod is ~25 nm and the size of the gold nanoparticle is ~30 nm in diameter. The corresponding electron diffraction pattern [Fig. 3(b)] shows that the growth direction was along [0001] and that the sidewalls are $\{01\bar{1}0\}$ faceted. In the high resolution TEM image shown in Fig. 3(c) taken from the center region of a ZnO nanorod, the dislocation-free crystal structure can be clearly seen and there is no amorphous layer covering the nanorod. Since the $\{01\bar{1}0\}$ facets of ZnO wurtzite structure are nonpolar surfaces, the bending cannot be attributed to a local dipole moment created by surface polarization.[9]

From these observations, a metal–semiconductor junction model is proposed to explain the self-attracting effect. It is known that gold and *n*-type ZnO can form a Schottky contact.[10,11] The work function of gold is 5.1 eV and our previous research revealed that the 1D ZnO nanostructure has a work function of 5.2–5.3 eV.[12] Thus, as illustrated in Fig. 4(a), the ZnO Fermi energy level is lower than that of gold because of its larger work function, so that electrons will flow from gold to ZnO during the formation of the metal–semiconductor junction to establish a constant Fermi energy level. This charge redistribution results in a positively charged Au particle and a negatively charged ZnO nanorod, with highest charge density region located adjacent to the junction.

When the ZnO nanorods are free standing, the electrostatic forces induced by the junction barrier are insufficient to overcome the elastic deformation force for bending. However, with the assistance of an external electron beam, electrons are excited from the valence band into the conduction band of ZnO. Thus, the electron concentration increases, whereas the holes in the valence band are filled by electrons flowing in from the Au tip, resulting in an increase in the local charge density on both sides of the Au/ZnO junction. Thus, the dipole moment increases even though some recombination of electrons with holes occurs in the ZnO. If the lengths of adjacent Au/ZnO nanorods differ, they will attract

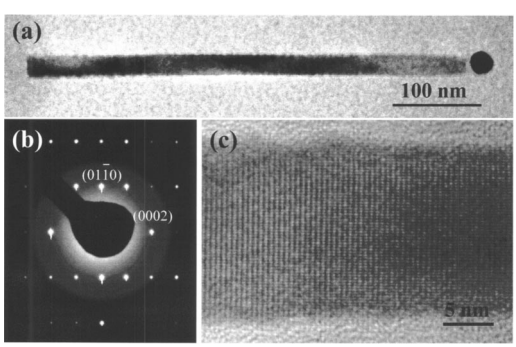

FIG. 3. (a) A low-magnification TEM image of a single ZnO nanorod; (b) corresponding diffraction pattern; (c) a high-magnification TEM image of the ZnO nanorod.

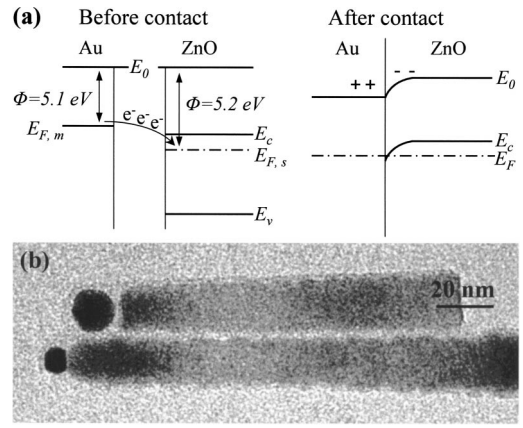

FIG. 4. (a) Band gap structure of a Au and ZnO junction. (b) Two freely contacting ZnO nanorods.

each other due to the asymmetric attractive and repulsive forces between them. Evidence to support this model is shown in Fig. 4(b), which shows two free contacting ZnO nanorods when one nanorod's Au tip contacts the other's body just below the junction. All of the freely contacting nanorods are similar to the one presented in Fig. 4(b). We have not found any two aligned nanorods that are contacted head-to-head and body-to-body. This is important for our proposed model.

The model proposed to calculate the magnitude of the forces responsible for the bending is shown in Fig. 5(a). Each Au/ZnO nanorod can be viewed as a dipole; the total force between two dipoles is attractive only if the nanorods have different lengths, such that the gold tip of one contacts the body of the other just below the junction interface. For free-standing nanorods, once the electrostatic attraction overcomes the elastic bending force, bending is possible.

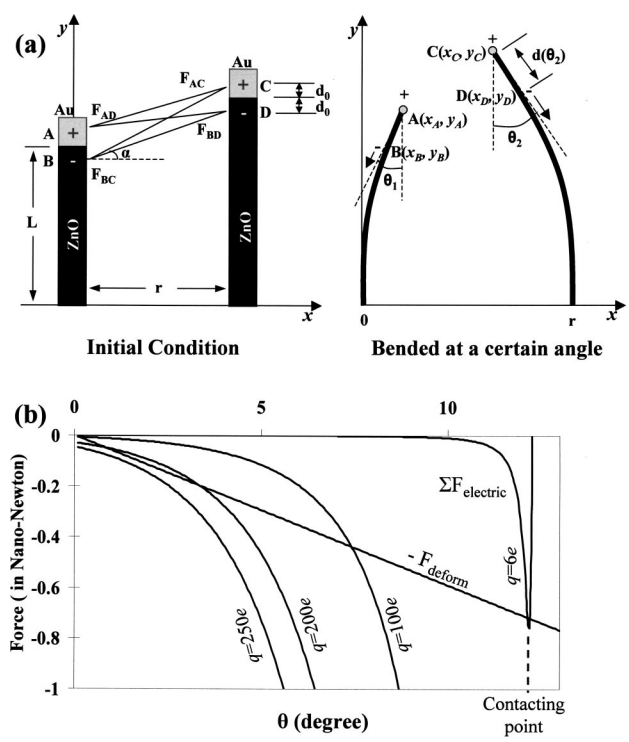

FIG. 5. (a) Schematic model of the interaction between two ZnO nanorods. (b) The calculated electric attraction force and elastic force based on bending angle.

To simplify the case, we just consider the interaction between two nanorods. The left side of Fig. 5(a) shows the initial state for two nanorods with lengths L_1 and L_2, respectively, separated by a distance r. The positive and negative charges are treated as point charges that are initially located the same distance from the Au/ZnO interface (points A and C for gold particles 1 and 2, points B and D for nanorods 1 and 2, respectively). This distance is represented by d_0. Now four different electric interactions exist: two forces of repulsion between like charges, F_{AC} and F_{BD}; two attractive forces between opposite charges, F_{AD} and F_{BC}. Assuming all the charges have the same magnitude, q, and considering only forces along the x direction are effective in bending the nanorods, each effective electrostatic force can be presented by Coulomb's equation:

$$F = \frac{q^2}{4\pi\varepsilon_0 R^2}\cos\alpha,$$

where ε_0 is the permittivity of space, R is the distance between two point charges, and α is the angle between the force and x axis. As shown on the right-hand side of Fig. 5(a), the bending angle θ, the angle between the y axis and the tangent at the nanorod tip, is used for defining any intermediate state during the bending process. The relationship between the bending angle θ and the force F required to overcome the induced elastic energy is $\theta = FL^2/2EI$, where L is the length, E is Young's modulus, and I is the moment of inertia of the ZnO nanorod with a hexagonal cross section.[13] Since there is no other external force, the bending forces experienced by the two nanorods must be equal. During bending, we assume that the positive charges are confined due to the very small size of the gold particles, whereas the negative charges can flow along the ZnO nanorods due to charge interactions. This is especially the case when the Au tip of one nanorod becomes close to the body of another nanorod. Then we can simply assume that the distance from the negative charge center to the interface increases linearlly with increasing bending angle,

$$d(\theta) = d_0 + \frac{\Delta L - d_0}{\theta_0}\theta,$$

where d_0 and ΔL are the initial and final distances from the negative charge to the interface and θ_0 is the bending angle at which the two nanorods are in contact. This assumption meets the condition that the center of negative charge on the ZnO nanorod is closest to the center of the positive charge on the other nanorod tip, when both are in contact.

The balancing of the electrostatic force and the elastic deformation force can be calculated. The curved lines in Fig. 5(b) are the electrostatic force calculated as a function of the bending angle for $L_1 = 400$ nm, $L_2 = 500$ nm, $r = 100$ nm, $d_0 = 10$ nm and $q = 6e$, $100e$, $200e$, and $250e$ ($e = 1.6 \times 10^{-19}$ C), respectively. The straight line is the elastic deformation force for a Young's modulus of $E_{\mathrm{ZnO}} = 50$ GPa.[14] This force is plotted in reversed sign in order to compare its magnitude with the electrostatic attraction force. The attractive force increases slowly for small θ and increases dramatically when the two nanorods are in close proximity. For a small electron concentration, forming a contact between two nanorods is unlikely (cases $q = 6$–$200e$). However, when the number of electrons exceeds 250, the attractive force becomes large enough to overcome the bending induced elastic force over the entire θ range. In this case, the ZnO nanorods are strongly attracted, and suddenly come together, as observed. Once the two nanorods are in contact, discharging may occur at the contacting point. However, short-range bonding such as van der Waals force can be induced that hold them together even days after the experiment.

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