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Photo-enhanced field electron emission of cadmium sulfide nanowires

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The response of field electron emission of cadmium sulfide (CdS) nanowires (NWs) to visible light has been investigated. It is found that, upon light illumination, the turn-on voltage drops, emission current increases obviously, and the Fowler-Nordheim behavior deviates from a straight line. A process of field emission coupled with semiconducting properties of CdS NWs is proposed. Photon-excited electron transition from the valence band to the conductance band of CdS nanowires increases the quantity of emitting electrons, and the photoemission decreases the effective work function of CdS emitters, which largely enhances the field emission performance. The response of field emission of CdS NWs to light illumination suggests an approach for tuning field emission of semiconductor emitters.

field electron emission, optical coupling, CdS nanowires, semiconductor emitters

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1 Introduction

Due to the unique electronic, optical and piezoelectric properties, cadmium sulfide (CdS) semiconducting nanowires (NWs) are considered an important multifunctional building block for fabricating various nanodevices, such as field effect transistor [1], lasers [2], waveguides [3], logic gates [4], sensors [5], nanogenerators and field emitters [6,7]. Although there is already abundant research on semiconducting and optoelectronic properties of the CdS NWs, the coupling among the field electron emission property, semiconducting and the optoelectronic property is rarely reported [8]. The pioneering work was reported on the field emission coupled with semiconducting property from CuO nanobelt arrays [9]. Such a kind of multifunctional coupling is not only significant for applications of CdS NWs in field emission and optoelectronics technologies, but also could throw light on their fundamental research, such as the internal electronic structure, the surface effect, and the optoelectronic transport [10].

In this paper, we have investigated the response of the field electron emission of CdS NWs to visible light. The Fowler-Nordheim (F-N) behavior deviates from a straight line upon the light illumination. And it is found that the turn-on voltage drops and the field emission current largely increases while CdS NWs are exposed under the visible light. The coupling between the field emission property and the semiconducting property of CdS NWs could play a key role in the tuning of field emission of semiconductor field emitters.

2 Methods

The CdS NWs were synthesized by the chemical vapor deposition (CVD) method, as reported in ref. [5]. The field

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electron emission measurements were carried out in a high vacuum chamber with a typical vacuum of 5×10^{-7} Pa [11,12]. The conductive substrate with CdS NWs was mounted on a metal base, and the NWs acted as a cathode. A molybdenum probe with a tip area of 0.8 mm^2, controlled by a stepper, was used as an anode. During our measurements the distance between anode and cathode was kept constant at 150 μm. The field emission characteristics of the CdS NWs were obtained by varying the applied voltage and recording the emission current by a Keithley 6485 electrometer at intervals of 1 s. The emission current-voltage characteristics were analyzed by the F-N equation for the field electron emission:

$$J = A\left(\beta^2 V^2 / \Phi d^2\right)\exp\left(-B\Phi^{3/2} d/\beta V\right), \tag{1}$$

where J is the current density, A and B are constant: A=1.56 $\times10^{-10}$ A V^{-2} eV, B=6.83×10^9 V $eV^{-3/2}$ V m^{-1}, β is the field enhancement factor, Φ is the work function, $E=V/d$ is the applied field, d is a distance between the anode and the cathode, and V is the applied voltage.

3 Results and discussion

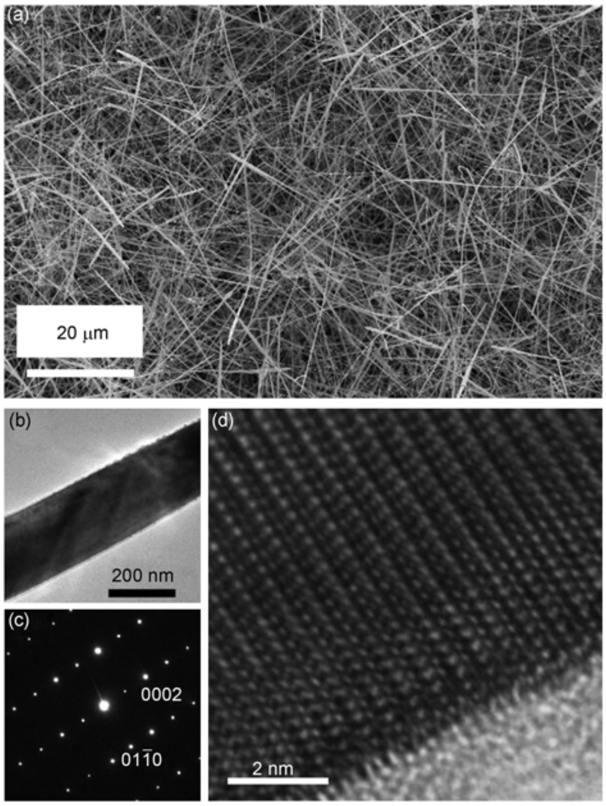

Figure 1 (a) A typical SEM image of the as-synthesized CdS NWs. (b) Low-magnification TEM image of a CdS nanowire. (c) The selected area electron diffraction (SAED) pattern, showing the nanowire grew along the ⟨0002⟩ direction. (d) A typical high-resolution TEM image of the CdS nanowires.

Figure 1(a) shows a typical scanning electron microscopy (SEM) image of the as-synthesized CdS NWs. The lengths of the NWs range from several micrometers to tens of micrometer, and the diameters range from tens of nanometers to hundreds of nanometers (Figure 1(b)). The CdS NWs are high-quality crystal and most of NWs grew along the ⟨0002⟩ direction, as revealed by electron diffraction pattern (Figure 1(c)) and high resolution transmission electron microscope (TEM) image (Figure 1(d)).

Figure 2 shows two groups of typical curves of emission current density vs. electric field (*I-E*) by varying the applied voltage, corresponding to the dark and light illumination condition, respectively, as indicated by the arrows inside the figure. Under each condition, the *I-E* curves were obtained by sweeping the voltage for two times. The coincidence of two curves for each condition indicates the quite stable field emission of the CdS NWs. Under the dark condition, the turn-on electric field was about 8.3 V/μm with current density of 0.1 μA/cm^2. The turn-on electric field dropped to 7.1 V/μm while a 40 W incandescent lamp illuminated outside the vacuum chamber. The lamp was about 30 cm away from the samples, and it illuminated the samples through a glass window of the chamber. The emission currents under light illumination are higher than those under the dark condition, as shown in Figure 2. With increasing the applied voltage, the curves of both conditions become closer, and they nearly coincide after the electric field larger than 14 V/μm.

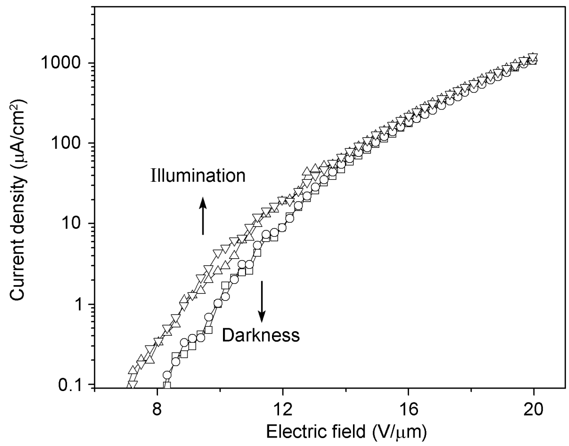

Figure 2 Curves of emission current density vs. applied electric field for a CdS nanowire film, corresponding to the dark and light illumination conditions, respectively, as indicated by the arrows inset.

Figure 3 shows the F-N plots, calculated from the *I-E* data in Figure 2. The F-N plot corresponding to the dark condition can be fitted to a straight line (as shown in the figure) in good agreement with the F-N equation, which confirms the field tunneling electron emission of the NWs. As indicated in Figure 3, the F-N plot corresponding to the light illumination condition deviates from the above straight line obviously in the region of lower voltage, while it tends

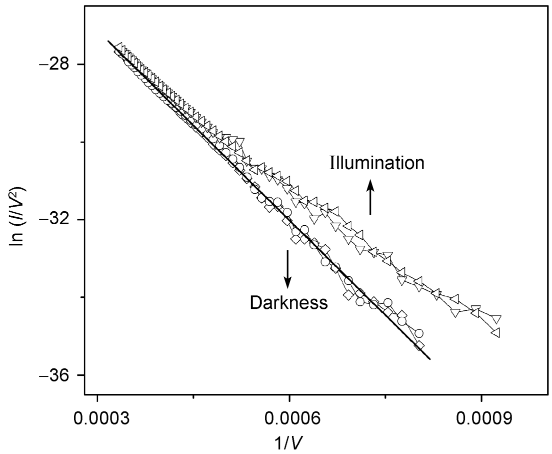

Figure 3 F-N plots obtained from the *I-V* data in Figure 2, corresponding to the dark and light illumination conditions, respectively, as indicated by the arrows inset.

to coincide with the one corresponding to the dark condition with increasing the applied voltage. According to the F-N theory (eq. (1)), the field emission property is determined by two parameters; one is field enhancement factor β, and the other is work function Φ [13]. Since field enhancement factor β is mainly related to the geometry of the emitters, the field enhancement factor of the CdS NW samples could not change upon the light illumination. The effect of light illumination on the work function Φ of CdS NWs could be the reason for the photo-enhanced field emission.

The energy band gap of CdS NWs is measured as about 2.4 eV, so the extra electrons can be excited from valence band of CdS NWs by the light illumination. From the semiconductor physics, the density of electrons n is in proportion to exp $\{-(E_C-E_F)/kT\}$ [14], where E_C is the bottom of conductance band and E_F is the Fermi level. The increase of electron concentration can result in the decrease of the value (E_C-E_F). And the relationship of the work function and energy band can be written as $\Phi=\chi+(E_C-E_F)$, where χ is the electron affinity. As it is different from the intrinsic work function, here, Φ is called effective work function. The increment of the electron density Δn under light illumination could lead to the decrease of the effective work function $\Delta\Phi$. Their relationship can be expressed as $\Delta n/n_0=\exp\{-\Delta\Phi/kT\}$, where n_0 is the initial electron density at the tip induced by the applied electric field. It is noted that the drop of effective work function only takes place at the emitting surface of CdS NWs. Previous theoretical studies on conducting needle-shaped conductors in the electric field also showed that the charging was located at their tips [15]. Such a phenomenon has been found from the carbon nanotubes in electric field by *in situ* TEM experiments [16]. In this work, the charging of CdS NWs could also exist in the emitting surface during the field emission process [17]. In the case of light illumination, the photo-generated electrons will accumulate at the emitting surface and then participate in the field tunnelling emission. Thus, the photo-induced increment in electron concentration leads to the reduction of effective work function at the emitting surface, which results in the decrease of turn-on voltage of field emission. Also, there are much more electrons (Δn +n_0) emitting into the vacuum, and thus, the field emission current increases.

The F-N plot corresponding to the light illumination condition deviates from a straight line, as indicated in Figure 3. The effect of light illumination on the field emission behavior is obvious in the region of lower voltage, which is attributed to the higher ratio between the numbers of photo-generated electrons and field emission electrons. With increasing the applied voltage, the ratio of the number of photo-generated electrons drops, and thus the influence of photoemission becomes weaker. And the F-N plot nearly coincides with the one under the dark condition when the voltage is larger than 2500 V (Figure 3), so the effect of light illumination can be ignored. It can be concluded that the F-N behavior under visible light is attributed to a process of field emission coupled with the optoelectronic property of CdS NWs.

Figure 4 shows the emission current trace by applying the pulsed illumination with a time interval of 20 s. The applied voltage is kept as 1000 V. For the first light illumination, the emission current increases gradually, then the emission currents demonstrate a series of stable cycles while the light is on and off continuously. The emission current increases from ~0.2 μA/cm^2 to ~0.3 μA/cm^2, i. e., an increase of ~ 50% is found at the applied voltage when light is on. The photo-tuned field emission could be used for designing the light sensor, and it also suggests a method for tuning field emission of semiconductor emitters. Moreover, other mechanisms, such as photodesorption effect [18], can be ruled out because the on/off emission currents are very stable. Further work on the wavelength-dependent photo-assisted field emission and the effect of irradiation dose is

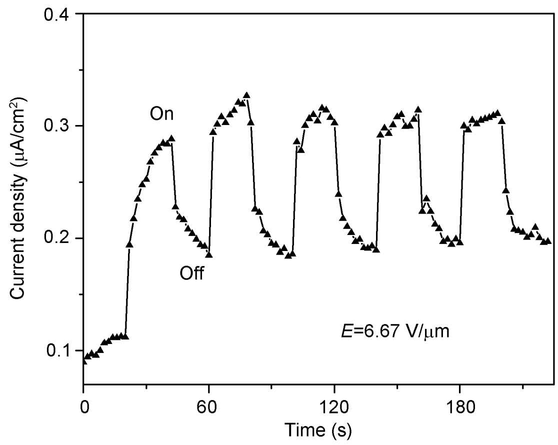

Figure 4 Response of the emission current to pulsed illumination. The time interval was 20 s, and the applied electric field was kept at 6.67 V/μm.

ongoing.

4 Conclusions

The effect of light illumination on the field electron emission of CdS NWs has been investigated. The results indicate that, upon light illumination, the turn-on voltage drops, and emission current increases obviously, and the F-N behavior deviates from a straight line. A process of field emission coupled with the optoelectronic property could be the mechanism for enhancing the field emission performance of the NWs. The photo-generated electrons lower the effective work function of the emitting surface, and they also act as a part of the emitting electrons, so the field emission is enhanced by light illumination. The photo-enhanced field emission of CdS NWs suggests a method for tuning the field emission properties of semiconductor emitters.

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