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Mechanical and Electrical Properties of ZnO-Nanowire/Si-Substrate Junctions Studied by Scanning Probe Microscopy

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Scanning tunneling spectroscopy was used to check the tunneling $I-V$ characteristics of junctions formed by n-ZnO nanowires deposited on Si substrates with n- and p-type electrical conductivity (i.e. n-ZnO nanowire/n-Si and n-ZnO nanowire/p-Si junctions, respectively). Simultaneously, several phenomena which influence the measured $I-V$ spectra were studied by atomic force microscopy. These influencing factors are: the deposition density of the nanowires, the possibility of surface modification by tip movement (difference in attraction forces between nanowires and the p-Si and n-Si) and the aging of the surface.

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1. Introduction

ZnO nanowires (ZnO NWs) are expected to play an important role as functional units in future nanoscale devices. Difficulty in reproducible p-type doping of ZnO (nominally undoped ZnO is of n-type) demands a method of electrical conductivity type verification which is cost effective and easy to perform. Scanning probe microscopy (SPM) has high spatial resolution and can probe local electronic properties of the material. Several interesting applications of SPM techniques on ZnO NWs were reported (conducting-atomic force microscopy (AFM) [1–3], NW bending [4], patterning growth locations [5]). In this work scanning tunneling spectroscopy (STS) is used for the identification of $p-n$ junction behavior of ZnO NWs on Si substrate. For n-ZnO NWs deposited on Si substrate, we expect — depending on the Si electrical conductivity type — the presence (for p-Si substrate) or the absence (for n-Si) of the tunneling $I-V$ curves of diode slope indicating the existence of $p{-}n$ junction. Besides these highly asymmetric ZnO/Si characteristics, we expect that at least two other kinds of $I{-}V$ curves ($I{-}V$s) should be measured: Si $I{-}V$s — asymmetric, different for n-Si and p-Si (as predicted in [6, 7]) and Si/SiO_x $I{-}V$s — for series connection Si/SiO_x on oxidized Si.

2. Experimental

The ZnO nanowires of length up to several micrometers and diameter up to several tens of nanometers grown by low pressure vapor phase transport process were mechanically scrapped off and deposited on two types of Si substrates: n-Si ($\rho = 0.025\ \Omega$ cm) and p-Si ($\rho = 0.02\ \Omega$ cm). All scanning probe microscopy measurements were performed on Nanoscope III di MultiProbe in air. The experiments were performed on as-deposited samples (AFM, STS), one day after deposition ("dynamic" STS on ZnO/p-Si), two weeks after deposition (manipulation of NWs), and approximately three months after deposition (AFM).

3. Results

The deposition density (i.e. the amount of the NWs on the area unit) of ZnO NWs on the substrate was estimated by AFM and is equal to several NWs per $(10\ \mu\text{m})^2$ for p-Si and less than 1 NW on $(20\ \mu\text{m})^2$ for n-Si. The dramatic difference in NWs deposition density on p-Si and n-Si is explained by huge differences in attractive forces between n-ZnO NW and p- or n-substrate. In the n-ZnO/p-Si junction a depletion layer is created and thus the attraction prevents the ZnO sliding by the AFM tip (Fig. 1a, b). On the contrary, the n-ZnO NWs are not stable on n-Si and can easily be moved by the AFM tip (Fig. 2a, b).

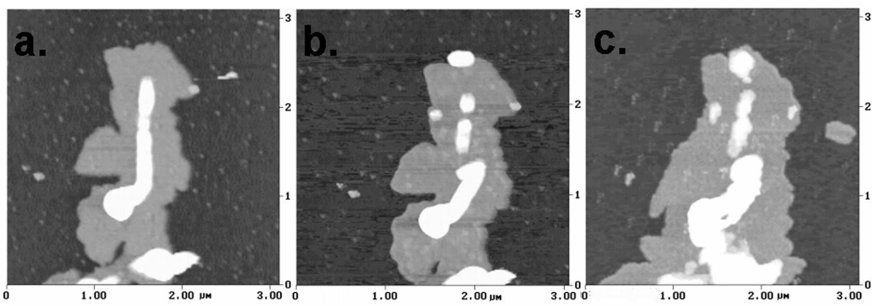

Fig. 1. n-ZnO NW/p-Si: (a) two weeks after deposition the NW is surrounded by an SiO_x island several nm thick; (b) after several attempts to move the NW to the right by the AFM tip the NW is broken into parts, the hard SiO_x island is undisturbed and the tip is damaged; (c) approximately two months after manipulation the surrounding SiO_x is slightly thicker and much wider, the broken parts of NW are overgrown by SiO_x and parts of the tip can be recognized as not surrounded by SiO_x layer.

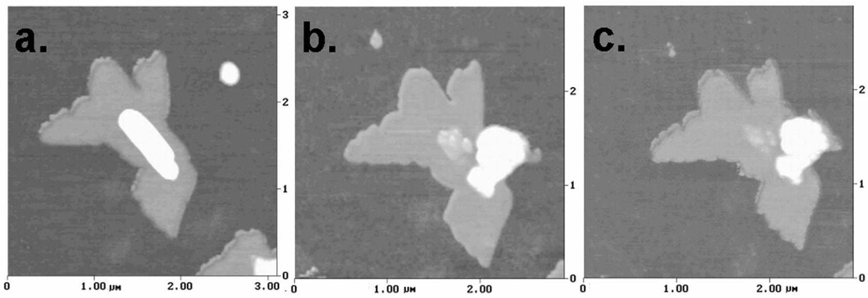

Fig. 2. n-ZnO NW/n-Si: (a) two weeks after deposition the NW is surrounded by an SiO_x island several nm thick; (b) the NW was easily moved to the right by the AFM tip but slightly broken, the SiO_x island is undisturbed; (c) next day after manipulation the surrounding SiO_x island has already overgrown the moved NW.

Scanning tunneling spectroscopy measurements (tip stabilized at a chosen point on the surface by tunneling parameters kept constant) performed on freshly prepared ZnO NW/n-Si samples result in two bundles of $I-V$ curves, where the curves in a bundle correspond to different tunneling distances (each curve is an average of 100 $I-V$s measured at the same position). These two bundles are identified as Si and Si/SiO_x characteristics, respectively (Fig. 3a). No $I-V$s which can be assigned to ZnO/Si tunneling were found, probably due to low deposition density and escape of the NWs from beneath of the tip.

In STS on as-deposited ZnO/p-Si samples again two $I-V$ bundles for Si and Si/SiO_x tunneling can be distinguished. Additionally, there are several curves of diode shape (Fig. 3b). Surprisingly, their onset value corresponds to the sum of Si (1.11 eV), ZnO (3.37 eV) and SiO_x (< 9 eV) onsets. This may be caused by a non-continuous contact of the NW to the Si surface and/or due to tunneling voltage drop in a large air gap.

The above results confirm the expected presence of diode slope $I-V$ curves on ZnO NW/p-Si junctions and their absence for n-Si substrate. Unfortunately, the ratio of the amount of the diode slope $I-V$ curves to the total measured $I-V$ curves is less than 1% despite the fact that the curves were measured at positions where a NW was observed. Moreover, it was only rarely possible to find a NW on a scanning tunneling microscopy (STM) (surface conductance) image. AFM examination of the ZnO/p-Si surface after STS measurements reveals that the NWs are swept out by the conductive STM tip. Therefore, another, "dynamic", $I-V$ measurement was applied. The scan angle was chosen to enable the tip to move parallel to the sample surface when the z-feedback was switched off (constant height mode). During the tip movement over a distance of several μm, the $I-V$s were measured. For ZnO/p-Si samples (Fig. 3c) four bundles of $I-V$ curves can be distinguished: two of them highly conductive (50% of total $I-V$s is assigned to Si tunneling and 40% of total $I-V$s is assigned to SiO_x tunneling) which might

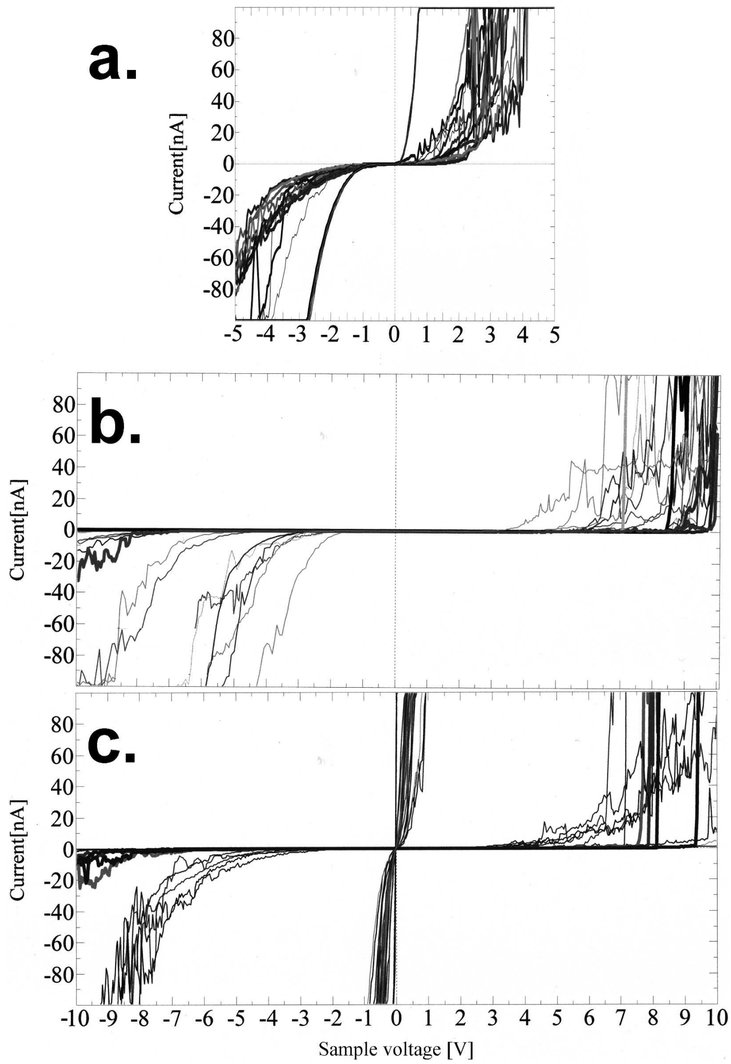

Fig. 3. Scanning tunneling spectroscopy $I-V$ characteristics: (a) n-ZnO NW/n-Si showing two bundles of curves corresponding to Si and Si/SiO_x tunneling; (b) n-ZnO NW/p-Si with several diode slope $I-V$s with abrupt current increase at onset voltage > 8 V; (c) n-ZnO NW/p-Si measured without z-feedback along a distance of several μm ("dynamic" STS) — the amount of diode slope curves corresponds to the possibility of NW trespassing on the distance driven by the tip.

correspond to the point contact between the tip and sample. The remaining 10% of total $I-V$s is less conductive and forms two bundles corresponding to Si/SiO_x tunneling and to $n-p$ (i.e. n-ZnO/p-Si) tunneling, respectively. As previously, the diode slope $I-V$ onset value of 7 eV is much higher than expected for ZnO/Si tunneling and again, weak contact between NW and Si and/or large air tunneling distance is the possible reason. The relatively high amount of $I-V$ curves exhibiting diode slope in the "dynamic" STS measurement confirms that the effect of NWs escape from the vicinity of the conductive tip is minimized.

In STS measurements there is a quite large amount of curves which correspond to SiO_x tunneling. At the day of NWs deposition the AFM images reveal uniform density of NWs which are lying directly on Si. Already next day after the deposition a less-conductive layer surrounding NW is detected by STM (for ZnO/p-Si) and can be easily seen on AFM images on one week old samples (Fig. 1a for ZnO/p-Si and Fig. 2a for ZnO/n-Si). The NWs are surrounded by continuously growing islands of SiO_x (absent on as-deposited samples). The islands grow only in the vicinity of NWs, in particular they overgrow the manipulated NWs (Fig. 1c and Fig. 2c). Their origin can be explained according to [8] by local oxidation of Si in air induced by electric field in the heterojunction. Additionally, this process is accelerated by UV light, when the photoinduced formation of hydrogen peroxide (and then H_2O_2 oxidizes the Si surface [9]) from oxygen in the presence of ZnO can occur [10]. The volume of the islands estimated from several the same relatively large surface areas scanned one week after deposition and two months later (for ZnO/p-Si) was increased by 30 vol%.

4. Conclusions

Electrical and mechanical properties of ZnO NWs depend on electrical conductivity type of Si substrate. For (n-)ZnO NWs deposited on p-Si the occurrence probability of $p-n$ junction $I-V$s was in agreement with the NWs deposition density. The formation of a depletion area in a $p-n$ junction results in high deposition density and limited n-ZnO NWs mobility on the p-Si surface. On the other hand, the electric field in a heterojunction (independent of Si substrate type) is high enough to favor the SiO_x layer growth in the vicinity of ZnO NWs. The comparison of the as-deposited and aged ZnO NWs/Si surface leads to the conclusion that reliable electric measurements can be performed on freshly prepared samples.

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