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Imaging mechanism of carbon nanotubes on insulating and conductive substrates using a scanning electron microscope

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Abstract Carbon nanotubes (CNTs) were deposited on bare glass, Au (10 nm)/glass, and Au (50 nm)/glass substrates, and observed using a scanning electron microscope (SEM) operating at different accelerating voltages. Depending on the substrate and accelerating voltage, the CNTs exhibit different levels of contrast. On the poorly conductive glass and Au (10 nm)/glass substrates, electrons are supplied or dissipated through the networked CNTs. This generates a potential difference between the CNTs and the (insulating or poorly conductive) substrates. CNTs are visualized as a result of potential contrast. At a low accelerating voltage (1 kV), the substrate is of higher potential than that of the networked CNTs (the ground potential), and the CNTs exhibit bright contrast. At a high-accelerating voltage (5–10 kV), the potential of the substrate is lower than the networked CNTs, and the CNTs exhibit dark contrast. On the Au (50 nm)/glass conductive substrates, the electrons are supplied through both the Au film and the CNTs, and topographic morphology of CNTs is observed.

Introduction

Carbon nanotubes (CNTs) are a unique type of nanostructured material suitable for future nanoscale electronics and sensors application due to their outstanding electrical and mechanical properties. Scanning electron microscope (SEM) is widely used for imaging CNTs. However, the image contrast of CNTs is very sensitive to SEM imaging conditions and substrate properties, because the electron beam interaction with them is negligibly small and the amount of secondary electrons (SEs) generated by a CNT is insufficient for imaging [1, 2]. On insulating substrates, CNTs can be easily imaged by SEM. The SE imaging of CNTs on an insulating surface was first reported by Brintlinger et al. [3] and later by Homma et al. [4]. Depending on the substrate on which CNTs are placed, CNTs exhibit either topographic contrast (on conductive substrates) or potential contrast (on insulating substrates) [5, 6]. Due to the small diameter and low atomic number, CNTs are hard to discern on conductive substrates. However, on an insulating substrate, the CNTs are much more easily seen at low voltages, where they appear very bright even at low magnification, and show an apparently larger diameter [7]. During SEM imaging at low accelerating voltages, the insulating substrate is usually positively charged, while at high accelerating voltage it charges negatively. Therefore, the potential difference is usually generated between the substrate and the CNTs. This potential difference either enhances or suppresses the emission of SEs from CNTs, which results in a distinct contrast between the CNTs and the substrate.

In this study, the surfaces of insulating glass substrates were modified by sputtering a thin Au film of different thicknesses (10 and 50 nm). CNTs were deposited on both modified and unmodified glass substrates, and observed under SEM operating at different accelerating voltages ranging from 1 to 10 kV. The coating of Au film alters the insulating nature of the glass surface, which can greatly affect CNT contrast during SEM imaging. In addition, to

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what extent the CNTs contrast is influenced by the thickness of the Au coating. The purpose of this study is to investigate the imaging mechanism of CNTs on different substrates. The influence of Au thickness and the accelerating voltage on CNT contrast is studied as well.

Experimental

Hydrous CNT dispersion with 1 wt% of CNTs (CarboDis ES, FutureCarbon GmbH, Germany) was diluted using deionized water into a stable suspension with a CNT concentration of 0.3 mg/L. A 200-nm pore size polycarbonate membrane (Isopore Membrane Filters, Millipore) was used to vacuum filter a 12-mL diluted suspension. After filtration, the membrane was transferred onto a glass substrate (microscope slides, Paul Marienfeld GmbH & Co. KG) with the CNT film side down and loaded with a 2-kg mass overnight to guarantee good attachment of CNTs to the substrate. Then the substrate together with the membrane was immersed in tetrahydrofuran to remove the polycarbonate membrane. Thus, a uniform CNT film deposited on glass substrate was obtained [8–10].

Some glass substrates were sputter coated with Au films of 10 and 50 nm, respectively. A CNT film was deposited on these Au/glass substrates using the method described above. After depositing the CNTs, several specimens were selected, and a polystyrene film of about 80 nm was spin coated onto the CNTs. All the specimens (with and without polystyrene coating) were examined using the SEM operating at different accelerating voltages (LEO 1530, Carl Zeiss GmbH, Germany). The in-lens detector which is situated inside the beam focusing lens was used. This detector excludes the backscattered electrons (BSE), the SE produced by high energy BSE which strike the pole pieces and other solid objects within the specimen chamber (SE3), and most of the SE produced by interactions of high energy BSE with specimen atoms (SE2), but has high efficiency in detecting the SE produced by the interactions of primary electrons from the incident beam with specimen atoms (SE1). In order to ground the CNTs, edges of CNT the film and the specimen mount were connected by silver paint.

A four-point probe was applied to measure the resistivity of the 10 and 50 nm Au films. The resistivity of Au film (ρ) was calculated using the following formula:

$$\rho = \frac{\pi t}{\ln 2}\left(\frac{V}{I}\right),$$

where t is the thickness of the film, V and I are the measured voltage and current, respectively.

Results and discussion

Imaging of CNTs on glass substrate

Deposited on a glass substrate, CNTs exhibit distinct bright contrast relative to the glass substrate at 1 kV (Fig. 1a). As the voltage increases to 2 kV, the CNTs still show bright contrast. However, the CNT edges appear to be darker than the substrate (Fig. 1b). A contrast inversion takes place at 5 kV, where the CNTs start to show dark contrast (Fig. 1c). This dark contrast is further enhanced at 10 kV (Fig. 1d). A careful examination of the images reveals that the CNTs which exhibit different contrast at different voltages are the networked CNTs. While the isolated CNTs (indicated by the frame) always show different contrast in comparison to the networked CNTs. Starting from 2 kV, the contrast of the isolated CNTs is independent of the accelerating voltage. Additionally, the diameter of these isolated CNTs appears to be smaller than that of the networked CNTs.

Under the bombardment of an electron beam, a specimen can be either negatively or positively charged depending on the SE yield (σ). The value $\sigma < 1$ suggests that the influx of primary electrons is greater than the amount of emitted electrons, and the specimen is negatively charged. Conversely, when σ is above 1, the specimen is positively charged. At 1 kV, the SE yield of SiO_2 is above 1, which suggests the glass substrate is positively charged [4, 11]. Electrons are supplied to the substrate through the grounded network CNTs. As a result of this flow, the network CNTs are of lower potential than the positively charged substrate, which enhances the local emission of SEs, and bright CNT contrast is observed [2, 4, 12]. As the accelerating voltage increases, the injected electrons exceed the emitted electrons. The substrate becomes negatively charged, making its potential lower than the grounded network CNTs. Therefore, the substrate exhibits bright contrast at 5 and 10 kV. The isolated CNTs always share the same potential with the glass substrate since there is no electron flow through them, and only topographic contrast is observed.

Imaging of CNTs on Au/glass substrate

On Au (10 nm)/glass substrate CNTs show similar contrast to those on the glass substrate (Fig. 2). The CNT contrast shifts from bright to dark as the accelerating voltage increases from 1 to 10 kV. Surprisingly, the Au grains located around the CNTs also exhibit the same bright contrast to the CNTs, which makes the identification of CNTs difficult. However, as a result of these bright Au grains, the arrangement of CNTs on the Au (10 nm)/glass substrate can be easily recognized. On Au (50 nm)/glass substrate, CNTs exhibit similar contrast at different

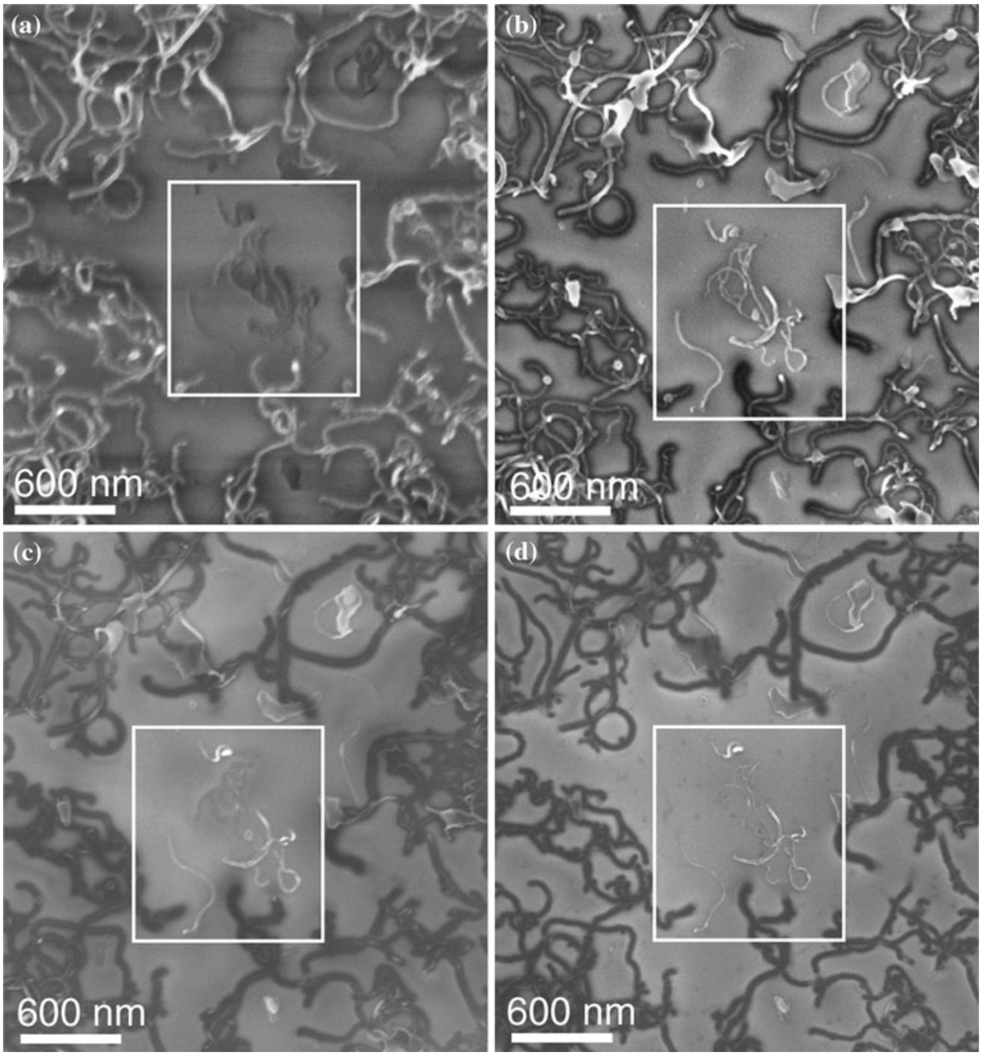


Fig. 1 SEM images of CNTs on glass substrate at **a** 1 kV, **b** 2 kV, **c** 5 kV, and **d** 10 kV

accelerating voltages. Even at 10 kV, the CNTs still appear to be brighter than the Au layer, which is obviously a topographic contrast (Fig. 3).

According to our measurements, resistivity of the 10 and 50 nm Au films are 1.96×10^{-7} and 1.29×10^{-7} Ω m, respectively, which suggests that the macro-resistivity of the two films is comparable. The 10-nm Au film in Fig. 4 exhibits a clustered structure with pores, voids, and channels in a nanometer scale, which suggests the glass substrate is not well covered by Au. Such structure was also observed by Fitting et al. [13] who characterized the submicron surface morphology of an Au film (8–12 nm thick) on a SiO_2 using a scanning tunneling microscope. In Fig. 4b, many cracks are observed for the 50-nm Au film (which can be described as brain-like structure), the film is rather complete and flat in comparison to the 10-nm Au film. On a micrometer scale, the clustered structure of the 10-nm Au might not influence the resistivity much. However, the pores, voids, and channels might influence the local electron transport on a nanometer scale. It is believed that the compensation of electrons through the 10-nm Au film is rather low. At 1 and 2 kV, the 10-nm Au film is positively charged, and the electrons are mainly supplied through the grounded CNT network and they exhibit bright contrast accordingly. Some electrons are able to spread from the highly conductive CNTs to the surrounding Au grains despite the pores and channels. These Au grains show bright. At 5 and 10 kV, the potential of 10 nm Au film is lower than that of the CNTs (the ground potential) because the injected electrons cannot be readily dissipated. The emission of SEs from the Au film is enhanced as a result of the lower potential, therefore dark CNT contrast is observed. A similar observation was also reported by Zhang who observed the conductive catalyst particles

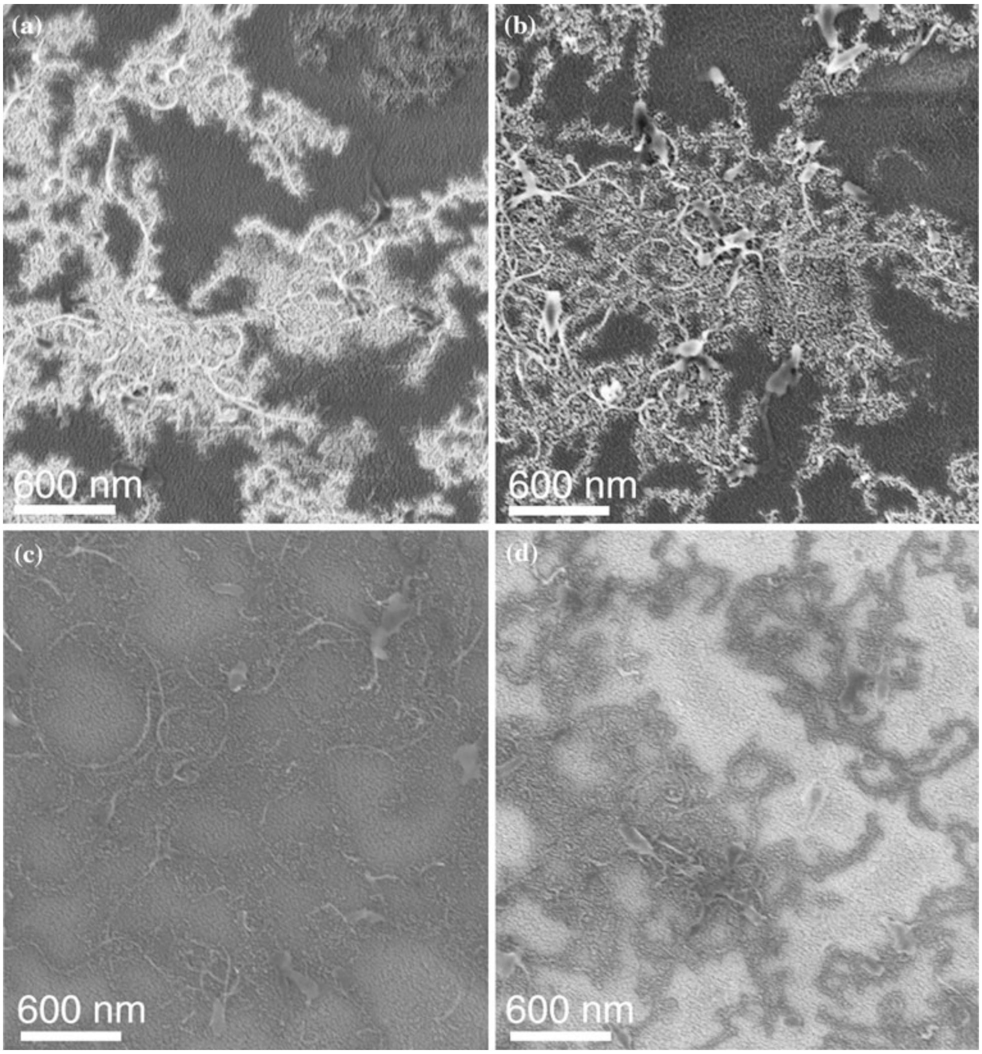


Fig. 2 SEM images of CNTs on Au (10 nm)/glass substrate at **a** 1 kV, **b** 2 kV, **c** 5 kV, and **d** 10 kV

around CNTs (which are connected to the metal pad) always exhibit the same contrast to the CNTs [2]. In addition, it is noticed that the dark contrast of CNTs and the neighboring Au in Fig. 2c is not as distinct as that in Fig. 1c. At 5 kV, the potential difference between the CNTs and Au (10 nm)/glass substrate is smaller than the potential difference between the CNTs and glass substrate in Fig. 1c, because of the conductive 10-nm Au film. Therefore, the image contrast is weaker.

The 50-nm Au film is a good conductor, electrons can be either supplied or dissipated through this film. Therefore, the CNTs and substrate are of the same potential, topographic morphology appears instead of the potential contrast image.

The imaging mechanisms of CNTs on different substrates are summarized and illustrated in Fig. 5. On a glass substrate, the potential difference between the networked CNTs and the substrate is always high and generates distinct CNT contrast. The isolated CNTs are of the same potential as the substrate and does not show voltage contrast. On the Au (10 nm)/glass substrate, networked CNTs and the surrounding Au grains are at ground potential (as indicated by the broken line). But the potential of the substrate could be higher or lower than the ground potential depending on the accelerating voltage. Therefore, the networked CNTs and the surrounding Au grains exhibit different contrast relative to the substrate. On the Au (50 nm)/glass substrate, there is no potential difference between the CNTs and the substrate, and only topographic contrast is observed.

Imaging of CNTs coated with polystyrene

CNTs deposited on glass, Au (10 nm)/glass, and Au (50 nm)/glass substrates were coated with a polystyrene

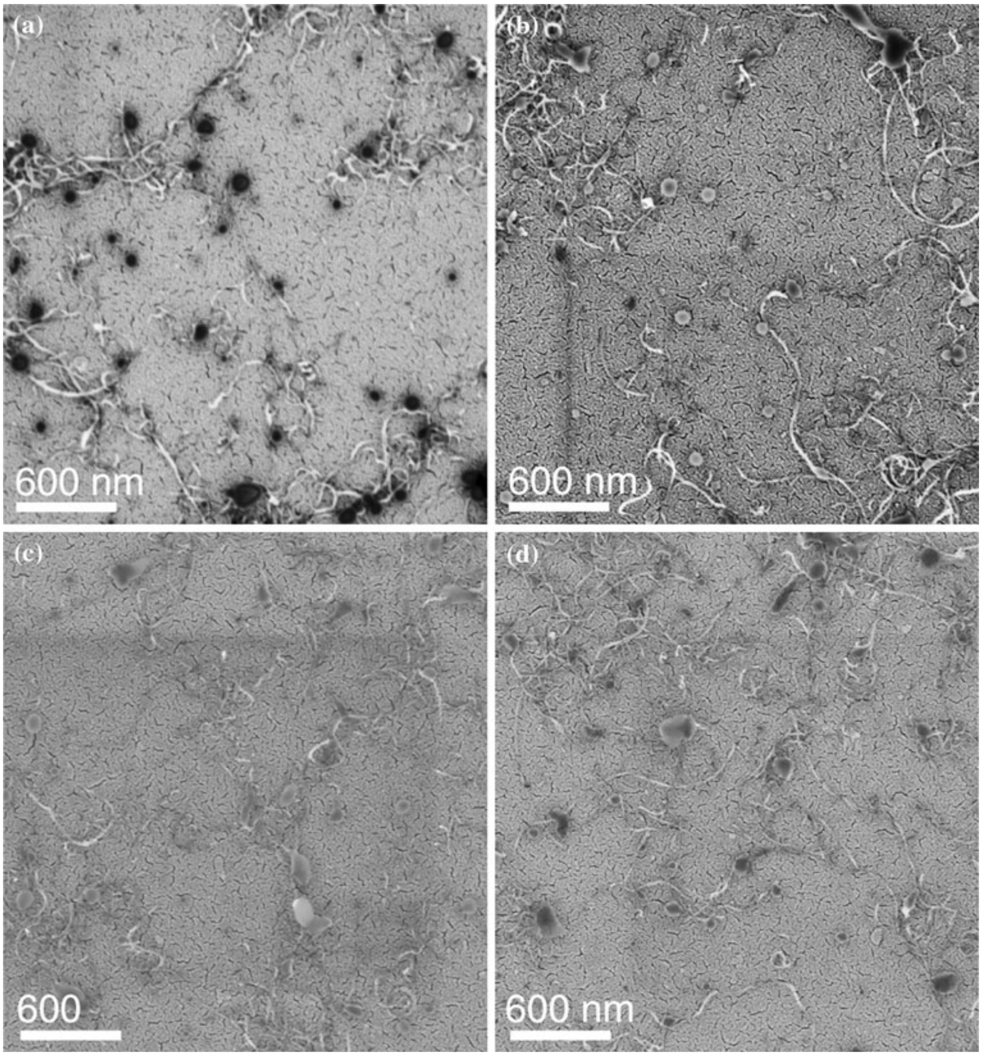


Fig. 3 SEM images of CNTs on Au (50 nm)/glass substrate at **a** 1 kV, **b** 2 kV, **c** 5 kV, and **d** 10 kV

film of 80 nm. The SEM images are presented in Fig. 6. No traces of CNTs can be detected at 1 kV irrespective of the substrates, only some dark dots are seen (Fig. 6a, c, e). At 10 kV, the CNTs which are deposited on the glass substrates are easily visualized despite of the polystyrene coating (Fig. 6b). While on Au/glass substrate, the CNT contrast is poor (Fig. 6d, f). Identification of individual CNTs on Au (10 nm)/glass is very difficult (Fig. 6d) although they still exhibit dark contrast. On the Au (50 nm)/glass substrate, the CNTs are not even visualized at 10 kV after coating with polystyrene (Fig. 6f). However, some uncovered CNT tips are noticed as indicated by the arrows. Obviously, distinct potential contrast between the CNTs and substrate on the open surface (Fig. 1d) guarantees good contrast for the polystyrene coated CNTs.

As seen in Figs. 2 and 3, CNTs are not always evenly deposited on the substrate, clusters are usually seen. During spin coating, the CNT clusters may not be completely covered by polystyrene. The dark dots in Fig. 6a, c and e correspond to the uncovered CNT clusters. At 1 kV, the penetration depth of primary electrons through polystyrene is estimated to be less than 40 nm (using the Kanaya and Okayama semiempirical expression [14]). Therefore, CNTs lying below the 80-nm polystyrene film cannot be visualized due to the low penetration depth. At 10 kV, polystyrene is highly negatively charged since the injected electrons far exceed the emitted SEs. In addition, the high energy electron beam even penetrates into the glass substrate and generates high negative potential which might spread to the polystyrene film as well. In the CNT-free regions, the high negative potential in polystyrene enhances local SE emission. However, on the glass substrate where CNTs are lying, electrons can be dissipated by conduction

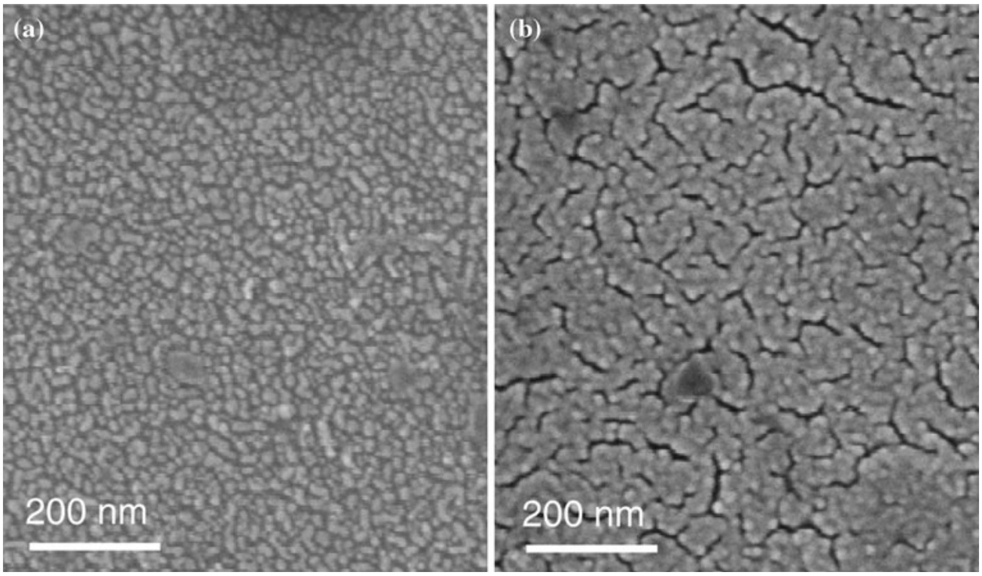
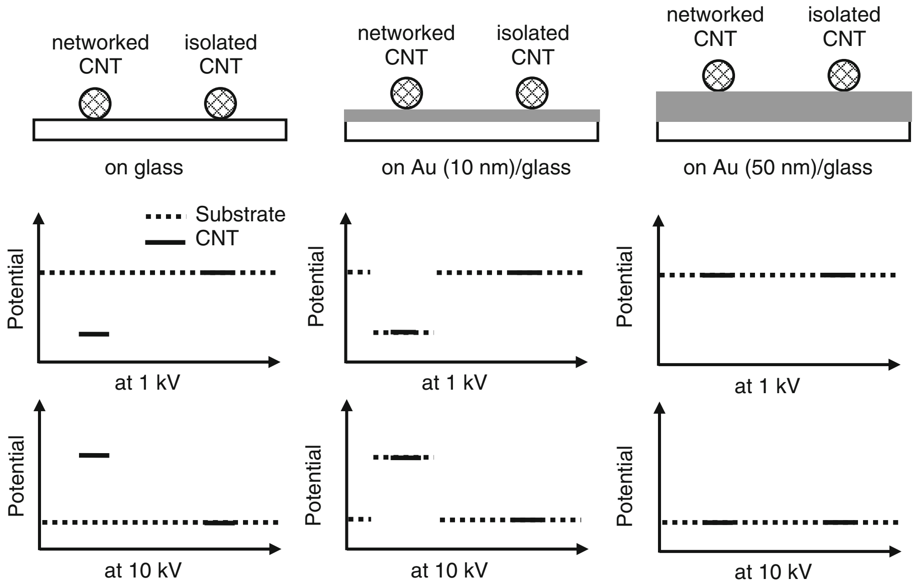


Fig. 4 SEM image of **a** 10 nm and **b** 50 nm Au film on glass substrate

Fig. 5 Illustration of imaging mechanisms of CNTs on different substrates



through the interconnected CNTs. Thus, the polystyrene above is less influenced by the charging glass substrate, and the SE emission from these regions is much lower and contrast is observed.

On the open Au (10 nm)/glass substrate, the Au grains around CNT exhibit the same bright contrast as CNTs (refer to Fig. 2d), which results in an even blurred CNT contrast after coating the polystyrene as shown in Fig. 6d. As Au thickness increases to 50 nm, the potential difference between CNT and Au film does not exist. The coated polystyrene exhibits a smooth surface without discernable contrast.

Conclusion

The imaging mechanism of CNTs on different substrates was investigated. It is found that CNTs exhibit different contrast on glass, Au (10 nm)/glass, and Au (50 nm)/glass substrates depending on the electrical conductivity of the substrates. The insulating nature of the glass is only slightly changed by the 10-nm Au coating; therefore on glass and Au (10 nm)/glass substrates, CNTs are observed as a result of potential contrast. The substrate is conductive with a 50-nm Au coating, the CNTs show topographic morphology. On an insulating substrate, the CNTs exhibit bright

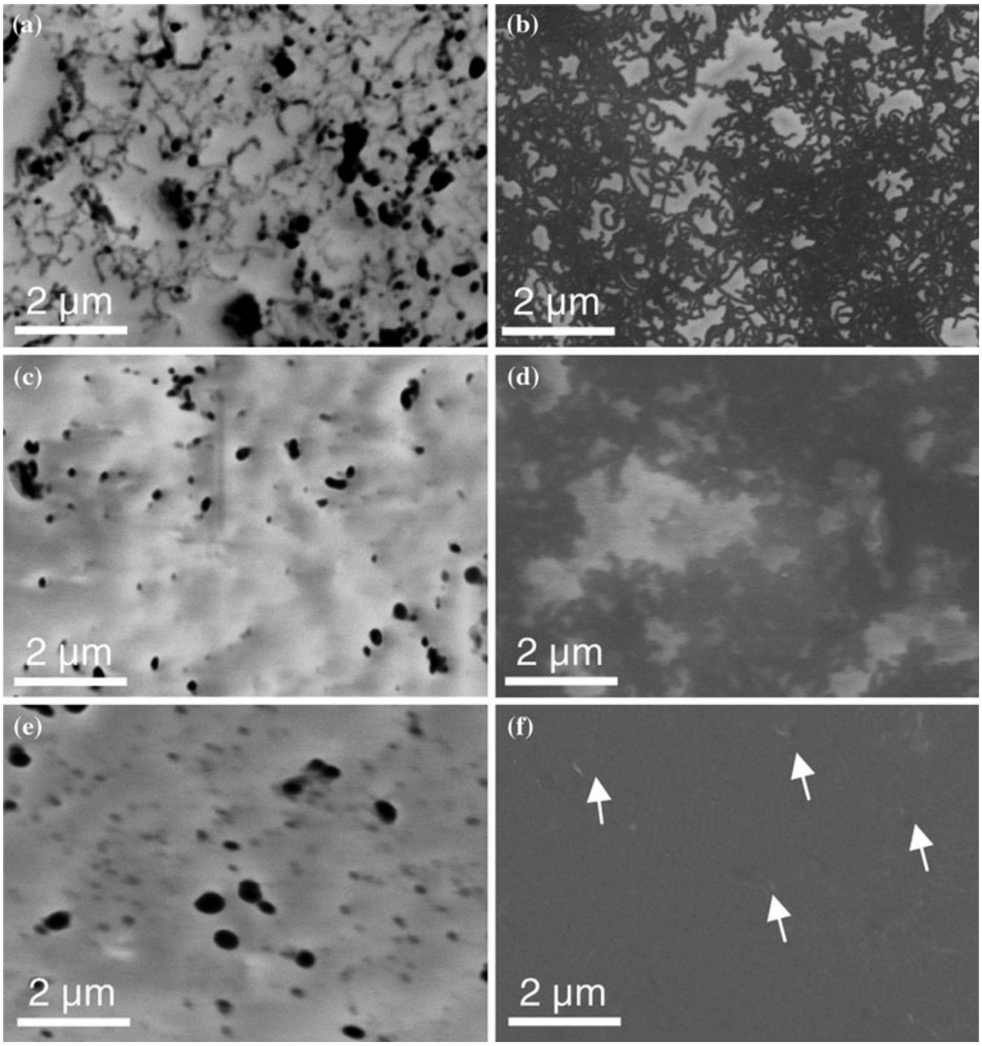


Fig. 6 SEM images of CNTs on different substrates coated with a polystyrene film of 80 nm. On glass substrate at 1 and 10 kV (**a**, **b**), on Au (10 nm)/glass substrate at 1 and 10 kV (**c**, **d**), and on Au (50 nm)/glass substrate at 1 and 10 kV (**e**, **f**)

contrast at low accelerating voltage and dark contrast at high accelerating voltages (>5 kV) as a result of electron flow through the CNTs.

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