Chapter 1 Introduction

1.1 Motivation

Presently, scanning probe microscopy (SPM) is widely used in the science research. Scanning tunneling microscopy is one of the SPM technologies utilized in investigating a large quantity of the metals and semiconductors on the atomic scale and the marvelous images of the world of atoms were created after the inception of the STM. Today, the STM is an invaluable asset in the surface research.

Despite the phenomenal success of the STM, it has a serious limitation. It requires electrical conduction of the sample material, because it uses the tunneling current, which flows between a biased tip and a sample. Hence, the atomic force microscopy was invented and can be used on the nonconductive substrate. Today, thousands of AFM are being utilized university, public and industrial research laboratories all over the world.

Noncontact atomic force microscopy (NC-AFM) is one mode of the AFM capable of achieving a higher resolution than intermittent mode and contact mode. NC-AFM is operated in ultra-high vacuum (UHV). The work principle of NC-AFM is based on the interactions between tip and surface. There are long range and short-range forces between tip and the surface.

In this thesis, the measuring error caused by the long-range force also known as electrostatic force was discovered. Such finding has imposed a challenge and consequently, on effective method needs to be defined to analyze the cause. Based on the research of this experiment, description of the long-range interaction supplemented with mathematical, scientific calculation, the NC-AFM has conclusively proven to be effective.

This research is found on the fundamental problems for those effects causing the image height errors by the non-contact AFM, and will provide some calculations and simulation. The lateral resolution of the AFM is determined by the size of the interaction region, which

depends on the sharpness of the tip and the range of the force interaction. In order to properly evaluate the images it is important to have knowledge of the shape and dimensions of the tip as the recorded data always has a dependency of the sample topography and the tip geometry. Techniques such as scanning electron microscopy (SEM) or transmission electron microscopy can be used to characterize the tip outside the AFM, but it would in many cases be favorable to obtain information about tip shape without removing it from the instrument.

1.2 AFM Review

In the last decade the atomic force microscope (AFM) invented by Binnig *et al.* experienced a significant transformation when a vibrating probe was used to explore the surface topography. Since then, dynamic AFM methods are emerging as powerful and versatile techniques for atomic and nanometer-scale characterization and manipulation of a wide variety of surfaces. True atomic resolution images of several semiconductor and insulator surfaces have also been reported.

At present, the application of atomic force microscopy in ultrahigh vacuum (UHV) has been widely spread as a powerful tool in surface science. The atomic force microscopy (AFM) can be followed in two different modes, by controlling the amplitude of the cantilever oscillation usually applied in air (AM mode), or by controlling the frequency shift Δf with respect to the free resonance frequency f_0 of the cantilever (FM mode, usually applied in vacuum). UHV AFM can always get higher resolution image than air AFM. Atomic force microscopy (AFM) was invented in 1986 by G. Binning and co-workers at Stanford University [1]. Since then it has successfully achieved many outstanding results on micro- and nanoscales and even on atomic and molecular scales.

Briefly trace the history of AFM as shown in Fig. 1.1. In 1986, Binning *et al.* invented AFM. In 1987, Binnig *et al.* succeeded in obtaining the lattice image of a graphite surface [2].

After that, AFM was believed to be an atomic resolution microscope even in the ambient atmosphere. In the same year, Mate *et al.* discovered that AFM works as a kind of frictional force microscope (FFM) and that AFM can obtain FFM images with lattice periodicity [3]. In 1990 Meyer and Amer [4] imaged, in ultrahigh vaccum (UHV), the lattice image of the NaCl(001) surface. Henceforth, UHV-AFM was believed to be an atomic resolution microscopy even in UHV. In 1991 Manne *et al.* showed that AFM could also contribute to atomic resolution studies of electrochemical reactions even in liquids [5].

Contact-mode AFM could not observe atomic defects such as atom vacancies and also that the normal load for typical AFM measurements considerably exceeded the load limit of a single atom. Therefore, the contact area for AFM measurement should be larger than the size of a single atom as shown in Fig. 1.2(a), implying that contact AFM does not provide true atomic resolution.

In 1992 Giessibl and Binnig [6,7] showed that a KBr surface in UHV was destroyed by scanning from the monoatomic step lines at the loading force of only approximately 1 nN and they succeeded in taking a step line image with atomic resolution in UHV at 4 K using contact AFM. Nevertheless, to demonstrate true atomic resolution of AFM more clearly, atomically resolved imaging of Si(111) 7×7 and atomic defects with STM-like reliability was required. In 1995 Giessibl [8] and Kitamura and Iwatsuki [9] succeeded in obtaining noncontact AFM (NC-AFM) images of the Si(111) 7×7 surface with atomic resolution in UHV at room temperature (RT) using a frequency modulation (FM) detection method [10]. This NC-AFM method detected a frequency shift in the mechanical resonant oscillation of the cantilever due to the attractive force between the tip apex atom and the sample surface atom, as shown in Fig. 1.2(b). Hence, using the FM detection method, NC-AFM in UHV was clearly able to demonstrate true atomic resolution under the attractive regime at RT.

Furthermore, in 1997, Uchihashi *et al.* demonstrated that the high contrast image on Si adatoms [11], i.e., it constitutes a kind of dangling bond image. An oxidized Si tip can reduce

chemical reactivity between the tip apex atom and the sample surface atom, so that by placing a suitable atom on the tip apex, they were able to control the atomic force between the tip apex atom and the sample surface atom, moreover, manipulating single atoms for creating artificial structures on surfaces [12].

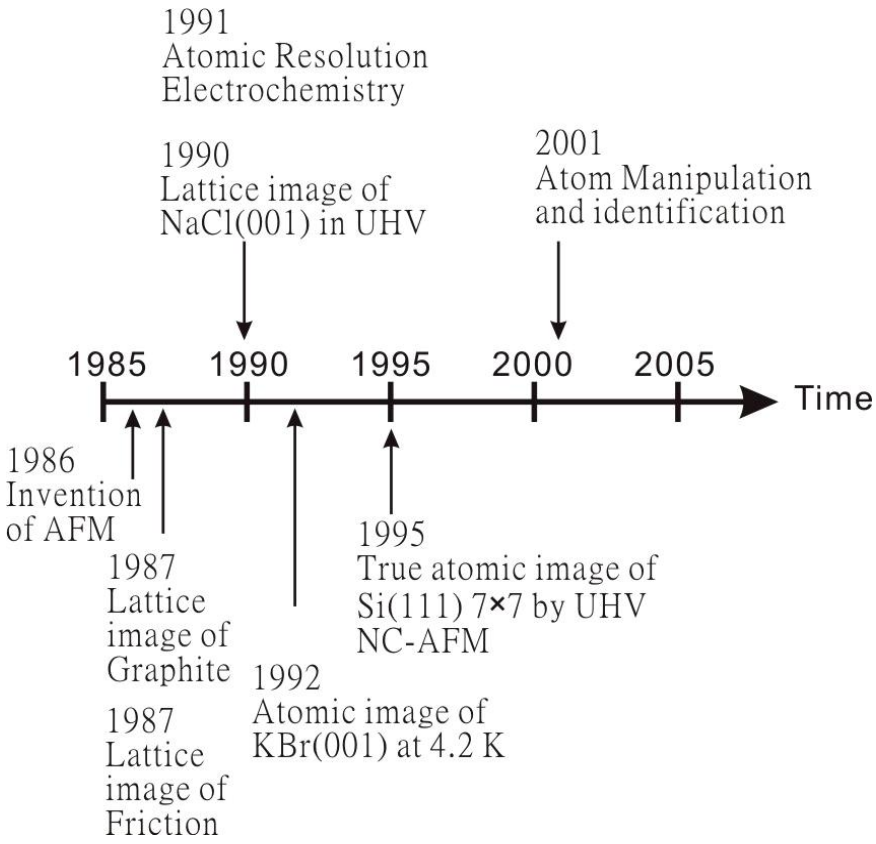

Fig. 1.1 Historical and present status for atomic force microscopy (AFM).

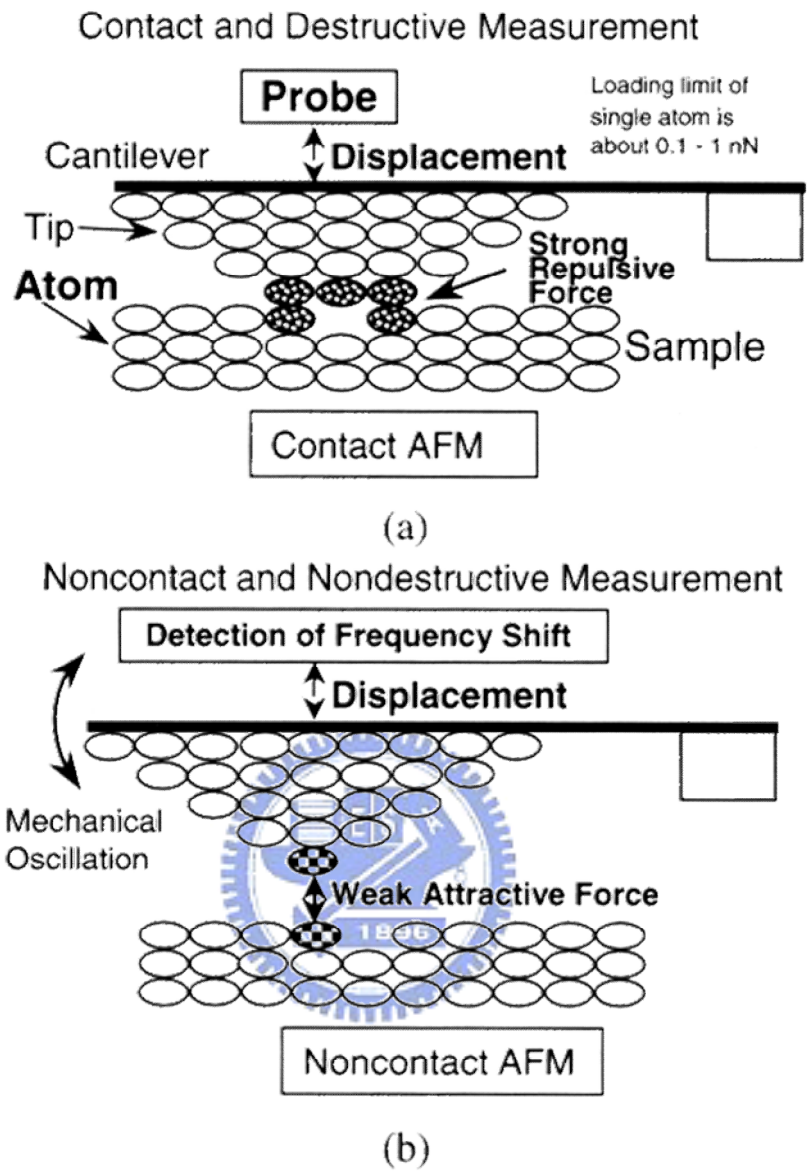

Fig. 1.2 Schematic models of (a) contact model AFM and (b) NC-AFM. (a) shows that contact model AFM is destructive and has a large contact area because of the strong repulsive force, while (b) illustrates that NC-AFM is nondestructive and can observe even an atomic point detect if weak attractive forces can be detected via a frequency shift in the mechanical oscillation of the cantilever. Copied from Noncontact Atomic Force Microscopy, edited by S. Morita *et al.* (Springer, Berlin, 2002).

1.3 The Role of the Contact Potential in Non-Contact AFM

According to the recent research, the surface topography measurement has become more and more important, as a result, the different measurement tool is being invented. For example, the atomic force microscopy (AFM) is among the powerful tool for measuring the surface and has the advantage in measuring nonconductive surfaces. The technique can also be extended to measure localized charges, magnetic distribution, as well as contact potential.

An electrostatic potential that exists between samples of two dissimilar electrically conductive materials (metals or semiconductors with different electron work functions) that have been brought into thermal equilibrium with each other, usually through a physical contact. Although normally measured between two surfaces which are not in contact, this potential is called the contact potential difference (CPD).

In this thesis, the contact potential plays an important role because it always active when the AFM scanned over the surface. Hence, the contact potential has to consider seriously, and takes an introduction. The contact potential difference (CPD) between two materials, for example, between an AFM tip and a sample, is defined as

$$V_{cp} = \frac{\Phi_{tip} - \Phi_{sample}}{-e}, \tag{1.1}$$

Where Φ_{tip} and Φ_{sample} are the work function of the tip and the sample, respectively, and e is the elementary charge. Therefore, if an AFM tip and a semiconductor with different work functions are held in close proximity to each other a force will develop between them, due to the potential difference V_{cp}; this is schematically described in the Fig. 1.3 [13].

When the two materials are not connected, their local vacuum levels are aligned but there

is a difference in their Fermi levels. Upon electrical connection the Fermi levels will align by means of electron current, as shown in Fig. 1.3(a). The two materials (electrons) are now charged and there is a difference in their local vacuum levels. Due to the charging of the tip and the sample, an electrostatic force develops as shown in Fig. 1.3(b). This force can be nullified by applying an external bias between the tip and the sample (see Fig. 1.3(c)). The magnitude of this bias is the contact potential difference and its sign depends on whether it is applied to the sample or to the tip.

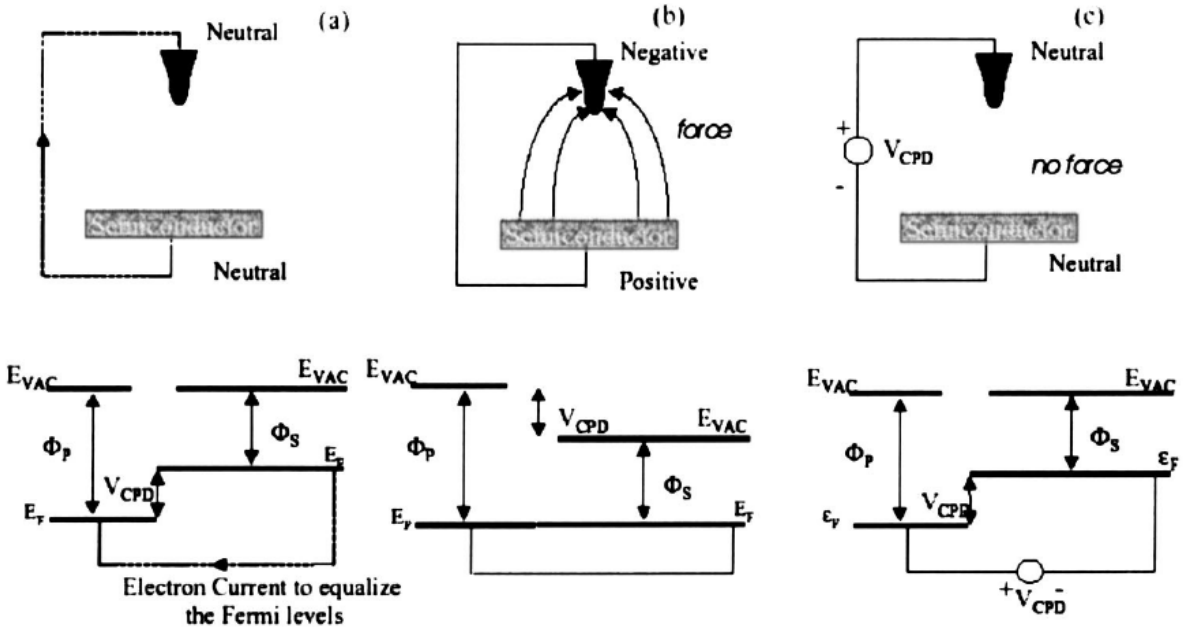

Fig. 1.3 Definition and basic measurement setup of contact potential difference (CPD). Copied from Y. Rosenwaks *et al.*, Phys. Rev. B 70, 085320 (2004).

1.4 Literature Review

Since the errors of measurement height were involved with tip shape and electrostatic force, we should present same papers to make a sense. Some researches have been published and discussed. Those papers showed the electrostatic force and tip apex effect from its measurement. The relative researches are described below according the publishing time.

In 1998, Olsson *et al.* present a method for *in situ* characterization of the tip shape in NC-AFM [14]. By sweeping the voltage between tip and sample and recording the sample position as it is regulated to give a constant force gradient as shown in Fig. 1.4. They can obtain information about the tip geometry from the curve of the sample position. The results show that the sphere model gives a good description of the interaction, and that the radii are consistent with data from scanning electron microscopy. The method can also be used to estimate the value of the Hamaker constant and the contact potential between tip and sample. The Hamaker constant of 1.8×10^{-18} J is a good fit in this experiment. This value is higher than those quoted for metallic systems ($3 - 5 \times 10^{-19}$ J).

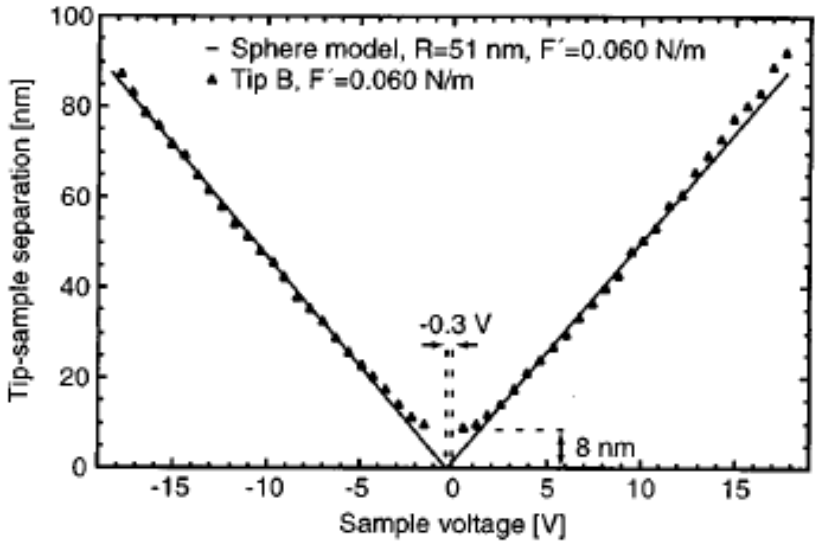

Fig. 1.4 The curve indicated by triangles show how the tip-to-sample separation *D* varies with sample voltages *U* at a constant force gradient of 0.06 N/m, using the B tip. The solid curve represents *D*(*U*+0.3 V) using the analytical expression for the sphere model describing the electrostatic interaction. The 0.3 V offset is due to the contact potential. Copied from Olsson *et al.*, J. Appl. Phys. 84, 4060 (1998).

In 2000, Guggisberg *et al.* demonstrated a system procedure for extracting parameters characterizing different type of interaction between a tip and a sample [15]. In a first step, the long-range electrostatic interaction is eliminated by compensating for the contact potential difference between the tip and sample. From the remaining long-range vdW contribution the tip radius can be estimated and used as a check on the tip shape. In the last step, the short-range interaction is determined by subtraction, and provides a measure of the range and strength of the bonding between the closest tip and sample atoms. The Hamaker constant ($H = 4 \times 10^{-19}$ J) that was fitted from the vdW interaction as shown in Fig.1.5.

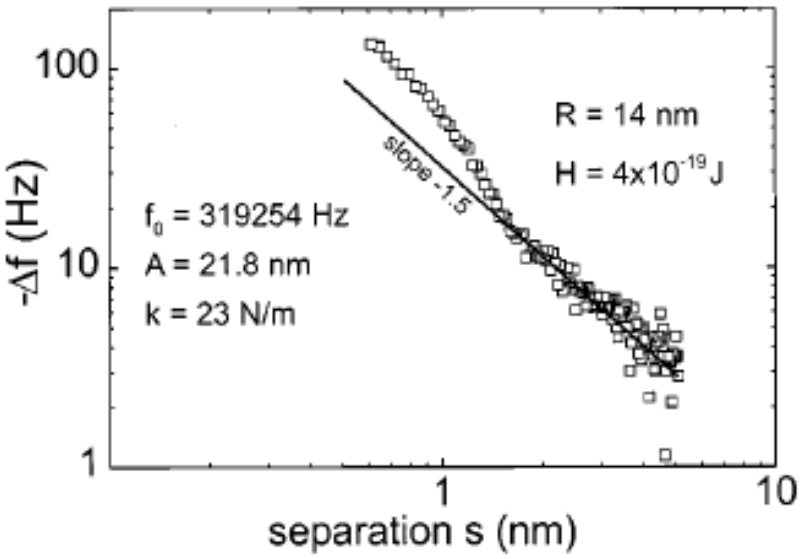

Fig. 1.5 Least-squares fit of the vdW contribution, assuming $\Delta f_{vdW} \propto s^{-3/2}$ in the range 1-6nm, where chemical interactions can be neglected. Copied from M. Guggisberg *et al.*, Phys. Rev. B 61, 11151 (2000).

In 2001, Colchero *et al.* analyzed the electrostatic interaction between a model probe and sample in a scanning probe microscope as shown in Fig. 1.6 [16]. A simple model for a real experimental setup is proposed and solved by means of an appropriate approximation. In addition, a quantitative definition for resolution is presented. The total force between tip and sample is demonstrated by contributions which are not confined to a nanometer-sized region under the tip apex. From the analysis they conclude that such a confinement is only obtained either with specially designed probes or by using the force gradient as signal source. Finally, an experimental setup was optimized resolution.

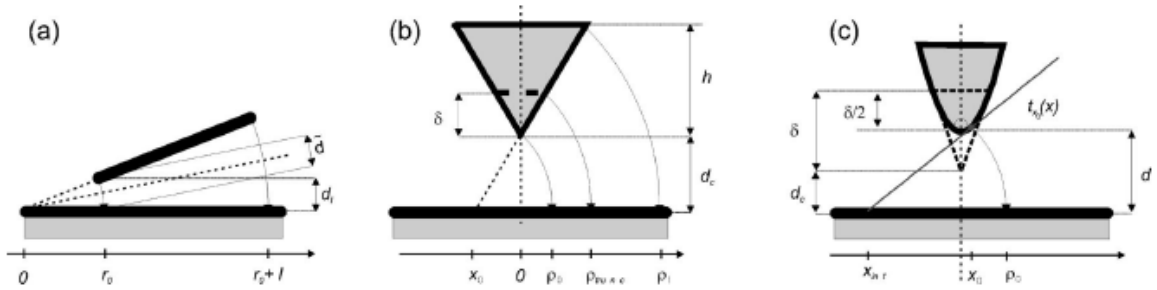

Fig. 1.6 Auxiliary sketches of (a) the lever-sample, (b) the cone-sample, and (c) the tip apex-sample system showing the parameters that are relevant for the calculation of the corresponding forces. Copied by J. Colchero *et al.*, Phy. Rev. B 64, 245402(2001).

In 2004, Sacha *et al.* presented a paper describing a method to determine the effective electrostatic tip radius of arbitrarily shaped conducting tips in atomic force microscopy as shown in Fig. 1.7 [17,18]. The method is based on the finding for conductive samples, the electrostatic force can be separated into two contributions: one from a constant background that depends only on the macroscopic shape of the tip (cone or pyramid and cantilever), and the other that depends only on the radius of curvature of the tip apex. Based on a simple theoretical expression derived from the generalized image charge method, conclusively showing that the tip radius can be directly determined from experimental force-distance characteristics. For irregular tip shapes, we show that the measured tip radius is the average of two principal curvatures, in agreement with tip shape images obtained by scanning electron microscopy.

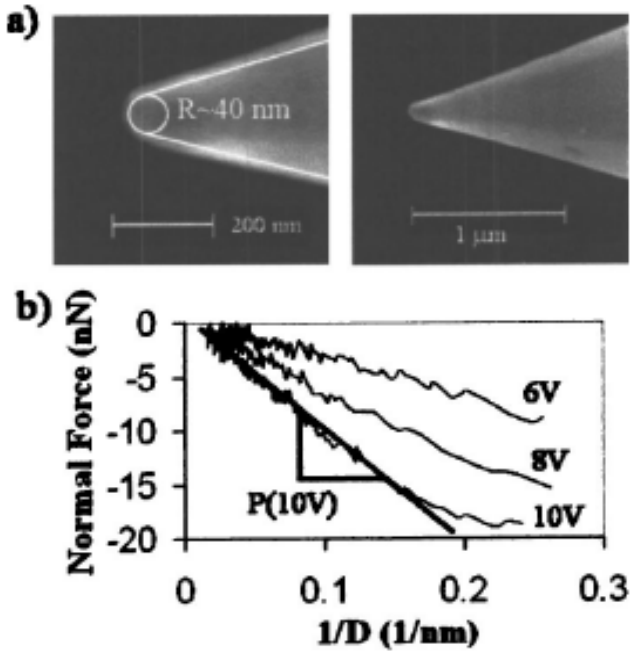

Fig. 1.7 (a) SEM images corresponding to the symmetrical tip A used in the experiments. The images show a conical shape ended at a sphere of R~ 40 nm. (b) Electrostatic normal force vs $1/D$ for different applied voltages. The calculated slope for R_{eff} = 35 nm tip and V = 10 V is also shown. Copied by G. M. Sacha *et al.*, Appl. Phys. Lett. 86, 123101 (2005).

In 2004, Sadewasser *et al.* presented the influence of uncompensated electrostatic forces on height measurements in NC-AFM, and demonstrates the correct height determination requires the use of Kelvin probe force microscopy (KPFM) with active control of the bias [19,20]. They use highly oriented pyrolytic graphite (HOPG) with a submonolayer coverage of C_{60} to HOPG as a function of dc bias for NC-AFM, and find a strong dependence of the step height on dc bias between tip and sample surface as shown in Fig. 1.8. The step height is modified by uncompensated electrostatic forces. In comparison, step from C_{60} to C_{60} or from HOPG to HOPG show no dependence on dc bias. The results clearly demonstrate the influence of uncompensated electrostatic forces on height measurements in NC-AFM.

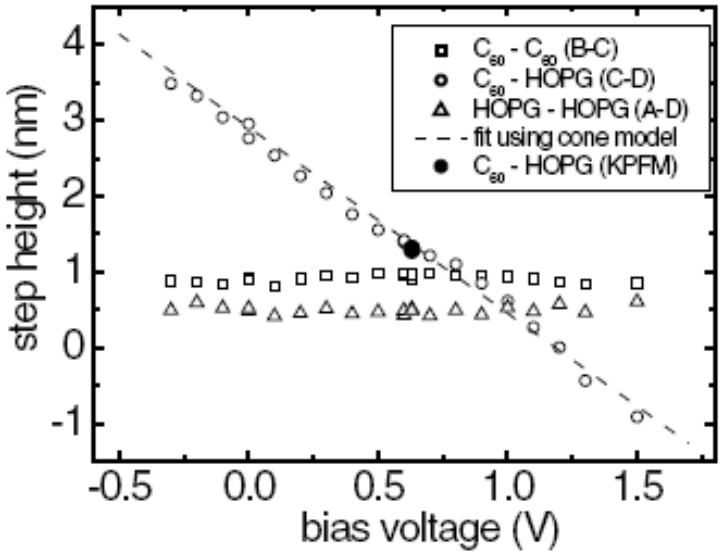

Fig. 1.8 Step heights as a function of V_{bias} measured by NC-AFM. Plotted are steps from HOPG to HOPG (open squares), C_{60} to C_{60} (open triangles) and C_{60} to HOPG (open circles). The step C_{60} to HOPG shows a strong bias dependence. The dashed line is a fit describing the electrostatic force between the tip (modeled by cone) and the surface. The solid circle represents the step height determined by KPFM. Copied from S. Sadewasser, Phys. Rev. Lett. 91, 266010-1 (2003).