# Atomic Dipole Moment Distribution of Si Atoms on a Si(111)-(7 × 7) Surface Studied Using Noncontact Scanning Nonlinear Dielectric Microscopy

Yasuo Cho* and Ryusuke Hirose

*Research Institute of Electrical Communication, Tohoku University 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan*

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A local atomic electric dipole moment distribution of Si atoms on Si(111)-(7 × 7) surface is clearly resolved by using a new technique called noncontact scanning nonlinear dielectric microscopy. The dc-bias voltage dependence of the atomic dipole moment on the Si(111)-(7 × 7) surface is measured. At the weak applied voltage of −0.5 V, a positive dipole moment is detected on the Si adatom sites, whereas a negative dipole moment is observed at the interstitial sites of inter Si adatoms. Moreover, the quantitative dependence of the surface dipole moment as a function of the applied dc voltage is also revealed at a fixed point above the sample surface. This is the first successful demonstration of direct atomic dipole moment observation achieved in the field of capacitance measurement.

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Broadly speaking, two types of scanning probe microscopy technologies have been reported to be capable of resolving real-space topography with atomic resolution: (i) scanning tunneling microscopy (STM) and (ii) atomic force microscopy. Although these techniques enable real atomic resolution imaging, they cannot directly distinguish the dipole moment of atoms making up the specimen to be measured without being supported by other speculative techniques [1–6]. For example, in a pioneering STM-based study, Hamers *et al.* obtained the first energy-resolved real-space images of surface states of the Si(111)-(7 × 7) surface [1], and Muralt *et al.* reported the first results on the microscopic potential distribution across a semiconductor heterojunction by means of scanning tunneling potentiometry [2]. They measured the surface states or the electrostatic potential by detecting the tunneling current, which can be categorized as a resistance measurement. However, such methods have only yielded circumstantial evidence for the existence of the dipole moment; the detected buildup of the electrostatic potential might also be due to a single monopole charge, other multipole charges, and/or a long-distance electrostatic potential distribution, etc.

The most direct method for observing an atomic dipole moment is the measurement of capacitance, rather than resistance or force, because the electrostatic capacitance has a one-on-one relationship to the absolute magnitude of dipole moments and its nonlinearity is related to the direction (polarity) of the dipole moment.

In recent years, we have developed and reported the use of scanning nonlinear dielectric microscopy (SNDM) for the measurement of the microscopic distribution of dielectric polarization [7–11]. Since the technique can sense the polarity of the specimen through the measurement of capacitance variation caused by nonlinear dielectric response, if we can resolve a single dipole moment of an atom, we can expect to be able to directly distinguish atomic species.

Equation (1) is a polynomial expansion of the electric displacement $D_3$ as a function of the electric field $E_3$ just under the tip.

$$D_3 = P_{s3} + \varepsilon(2)E_3 + \frac{1}{2}\varepsilon(3)E_3^2 + \frac{1}{6}\varepsilon(4)E_3^3 + \cdots \quad (1)$$

where $P_{s3}$ is spontaneous polarization, and $\epsilon(2)$, $\epsilon(3)$, and $\epsilon(4)$ are linear, lowest-order nonlinear, and higher-order nonlinear dielectric constants, respectively. (The number in parentheses denotes the rank of tensor.)

The even-rank tensors, including $\epsilon(2)$ and $\epsilon(4)$, are insensitive to the state of spontaneous polarization. By contrast, $\epsilon(3)$ is very sensitive to spontaneous polarization $P_{s3}$. For example, there is no $\epsilon(3)$ in materials with a center of symmetry, and the sign of $\epsilon(3)$ changes with the inversion of spontaneous polarization. Thus, by detecting $\epsilon(3)$ microscopically, we can measure the distribution of polarization.

The ratio of derivative capacitance variation $\Delta C_s$ [which varies with time because of the nonlinear dielectric response under the applied alternating electric field $E_{p3}(=E_p \cos\omega_p t)$] occurring just under the metal tip to the static value of the capacitance $C_{s0}$ ($C_s = C_{s0} + \Delta C_s$) is given by the following equation:

$$\frac{\Delta C_S}{C_{S0}} = \frac{\varepsilon(3)}{\varepsilon(2)} E_p \cos(\varepsilon_p t) + \frac{1}{4}\frac{\varepsilon(4)}{\varepsilon(2)} E_p^2 \cos(2\varepsilon_p t) + \cdots. \quad (2)$$

This equation shows that the alternating capacitance of different frequencies corresponds to each order of the nonlinear dielectric constant. Signals corresponding to $\epsilon(3)$ and $\epsilon(4)$ are obtained by setting the reference signal of the lock-in amplifier of the SNDM system to a frequency equal to $\omega_p$ and $2\omega_p$ of the applied electric field, respectively.

Equations (1) and (2), which use the dielectric constants, offer a somewhat macroscopic description. However, even if a very localized saturation is considered, for example, of atomic resolution, as the localized dipole moment also causes capacitance variation, Eqs. (1) and (2) are still applicable by replacing the electric displacement $D$ (or the polarization $P$), averaged electric filed $E$, and macroscopic dielectric constant $\varepsilon$, with the dipole moment $p$, local electric field $E_{\text{local}}$ (or $V_{\text{local}}$), and local polarizability factor $\varepsilon_{\text{local}}$, of a single dipole moment, respectively.

We have recently developed a noncontact scanning nonlinear dielectric microscopy (NC-SNDM) system operated in ultrahigh vacuum in order to prove that NC-SNDM has real atomic resolution. Using this microscopic technique, we have succeeded in observing the Si(111)-($7 \times 7$) atomic structure [12]. This is the first successful demonstration of atomic resolution in a dielectric microscopic technique. Unfortunately, the quality of the image in Ref. [12] falls far short of clearly distinguishing a single-atom dipole moment. Nevertheless, advances in the resolution of SNDM have been expected to enable improved characterization of the single dipole moment at the atomic level.

In this Letter, we clearly resolve the local atomic dipole moment distribution of Si atoms on Si(111)-($7 \times 7$) surface by NC-SNDM under ultrahigh vacuum (UHV) conditions. For this experiment, we have selected three types of Si samples ($p$-type Si with a resistivity of 0.01 $\Omega$ cm, $n$-type 0.003 $\Omega$ cm, and nondoped intrinsic Si) as the specimen and two types of metal tips (Pt-Ir tip and $W$ tip with different work functions). However, we have observed no significant difference among the samples and tips. As described in detail below, this implies that the data below are not related to conduction carriers in the semiconductor and the work function of the metal tip, but rather to the dipole moment composed of fixed charges on the Si surface.

First, the dc-bias voltage dependence of the atomic dipole moment on Si(111)-($7 \times 7$) surface was measured. Figure 1 shows the bias voltage dependence of the local dipole moment induced on the Si(1,1,1) surface. All measurements were performed under UHV conditions ($<1.0 \times 10^{-10}$ Torr). The typical tip radius used in this study was approximately 10–50 nm. The bias voltage was applied to the bottom of the specimen, and the tip was grounded, so that the application of a positive bias voltage induced a positive dipole moment in the upward direction. For the simultaneous detection of the SNDM signals of $\varepsilon_{\text{local}}(4)$ and $\varepsilon_{\text{local}}(3)$, an alternating voltage of 3 $V_{p\text{-}p}$ at 30 kHz was applied between the tip and specimen. The upper images in Fig. 1 show the topography from the $\varepsilon_{\text{local}}(4)$ signal in which individual Si atoms were observed. Moreover, a positive sign of $\varepsilon_{\text{local}}(3)$ signal indicates an increase in capacitance $C$ caused by dipole moment elongation, and the red color of the $\varepsilon_{\text{local}}(3)$ signal [12] shows that the direction of the dipole moment is positive (upward), while blue indicates a negative dipole moment.

In the figure, from left to right, the bias voltage was varied from $-1.0$ to 0.5 V in increments of 0.5 V. Although

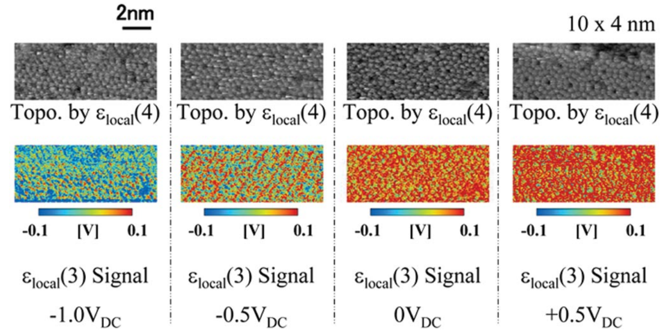


FIG. 1 (color). Bias voltage dependence of local dipole moment induced on the Si(1,1,1) surface. From left to right, the applied dc voltage was varied from $-1.0$ to 0.5 V in increments of 0.5 V. The upper images show the topography from the $\varepsilon_{\text{local}}(4)$ feedback signal in which individual Si atoms were observed. The lower images show the $\varepsilon_{\text{local}}(3)$ signal in which the red color of the $\varepsilon_{\text{local}}(3)$ signal shows that the direction of dipole moment is positive (upward), while the blue color of the $\varepsilon_{\text{local}}(3)$ signal shows that the direction of dipole moment is negative (downward).

Si is a dielectrically isotropic material with no spontaneous polarization from the averaged macroscopic viewpoint, the $\varepsilon_{\text{local}}(3)$ signal, which reflects the local anisotropy of the material, produces a meaningful contrast because all atoms in condensed matters are composed of positive atomic nuclei and negative electrons and they form a local dipole moment at the atomic scale. With increasing applied voltage, the dipole moment of Si atoms at the surface is polarized in the positive (upward) direction. Thus, the color of the $\varepsilon_{\text{local}}(3)$ mapping image shifts to red, where all atoms are polarized in the "up" direction at applied voltages above zero. Even at zero applied voltage, almost the entire surface is positively polarized with a strong red contrast reflecting the distribution of adatoms. This can be explained by the fact that the natural Si(111)-($7 \times 7$) surface is composed of top positive Si nuclei and the negative electrons making up the covalent bonding just below the surface Si nuclei and thus, overall, the Si(111)-($7 \times 7$) surface has a positive local dipole moment.

At the weak applied voltage of $-0.5$ V, we obtain the most distinctive contrast between the Si adatom site and the remaining area. Thus, we obtained magnified images (see Fig. 2) under the same bias condition of $-0.5$ V. A positive dipole moment was detected on the Si adatom sites, whereas a negative dipole moment was observed at the interstitial sites of inter Si adatoms. Upon bias voltage application, the head of dipole moments in interstitial sites of Si adatoms is switched to the negative direction. At this point, under a bias voltage of $-0.5$ V, the average value of the polarization of the Si(111) surface becomes almost zero by the cancellation of positive and negative dipole moments.

Figure 3 shows the one-dimensional image of topography and $\varepsilon_{\text{local}}(3)$ (both $\cos\theta$ and $A\cos\theta$), which were taken along the white line in Fig. 2. Amplitude $A$ is proportional

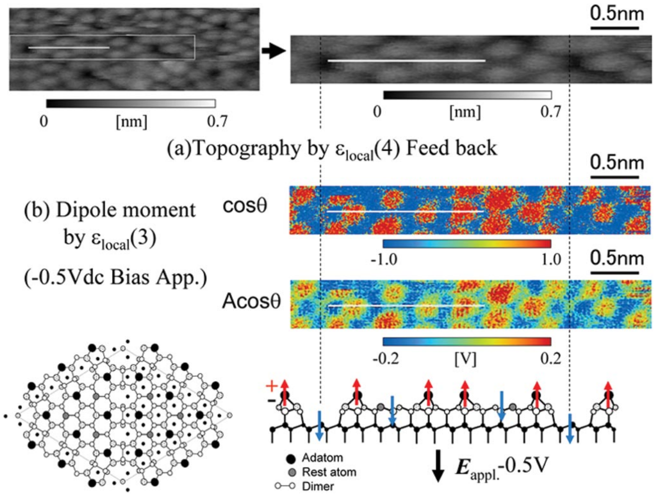


FIG. 2 (color). (a) Topographies taken by the $\varepsilon_{\rm local}(4)$ signal used as the feedback signal with an applied bias voltage of $-0.5$ V. (b) Magnified $\varepsilon_{\rm local}(3)$ images of Si adatoms obtained simultaneously with the topography.

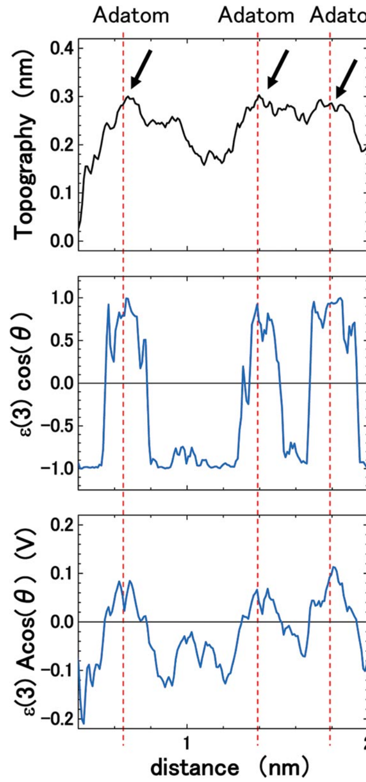


FIG. 3 (color). One-dimensional image of (a) topography and $\varepsilon_{\rm local}(3)$ [both (b) $\cos\theta$ and (c) $A\cos\theta$], which were taken along the white line in Fig. 2 at a bias voltage of $V_{\rm dc} = -0.5$ V. The vertical axis of topography represents relative height. The arrows in Fig. 3(a) indicate the adatoms. The $\cos\theta$ image shows the sign of the $\varepsilon_{\rm local}(3)$ signal to extract the polarity of dipole moment only. The average value of the $\varepsilon_{\rm local}(3)$ signal in (c) is almost zero.

to the absolute value of $\varepsilon_{\rm local}(3)$ and $\theta$ is the phase output from the lock-in amplifier in the SNDM system, which reflects the direction of the dipole moment. The $\cos\theta$ image [Fig. 3(b)] shows the sign of the $\varepsilon_{\rm local}(3)$ signal to extract the polarity of the dipole moment only ($\cos\theta = 1$ indicates that the direction of the atomic dipole moment is purely up, while $\cos\theta = -1$ means in the purely "down" direction, and the $A\cos\theta$ image [Fig. 3(c)] is more informative of the relative magnitude of dipole moments as well as their polarities. A comparison of Figs. 3(a) and 3(b) clearly reveals that a single positive dipole moment was detected at the adatom site indicated by arrows in Fig. 3(a).

Finally, the quantitative dependences of the lowest-order nonlinear dielectric signal [$\varepsilon(3)_{\rm local}$ signal], higher-order nonlinear dielectric signal [$\varepsilon(4)_{\rm local}$ signal] and tunneling current are measured as functions of applied dc-bias voltage at a fixed point above the sample surface, as shown in Fig. 4. In this case, the tip height (about 0.4 nm) was slightly larger than the tip height needed to detect the atomic dipole moment (about 0.08 nm), on the basis of our measurements on Figs. 1–3. Moreover, the tip radius (0.75 $\mu$m) used in the local spectroscopy mode was much larger than that in the scanning mode (typically 30 nm in radius). Thus, the value obtained from Fig. 4 reflects an averaged phenomenon, rather than a measurement taken on a single atom. It reveals that the Si(111)-(7 × 7) surface is naturally biased with an offset potential of $-0.6$ V, which is close to $-0.5$ V. This is consistent with the results shown in Fig. 2. It seems that the $\varepsilon_{\rm local}(3)$ signal is a cubic function with a bias (offset) voltage of $-0.6$ V, while $\varepsilon_{\rm local}(4)$ is a quadratic function with the same bias (offset) voltage. The tunneling current, on the other hand, is well-known to be a quasi-odd function with no offset value because there is weak asymmetry in the tunneling effect [13].

This implies that the average value of the dipole moment $P$ (surface polarization) can be written as a function of the applied voltage $V$, a power function of at least fifth order. If the atom is electrically isotropic, there is no specific direction in the atom and no even-power function in the $P$-$V$ relationship, which is, by definition, symmetrical at the origin. Thus, there is no even-order effect in the $P$-$V$ relationship:

$$P \propto a' V^5 + a'' V^3 + a''' V. \quad (3)$$

However, in this case, even at zero applied voltage, the surface of Si(111)-(7 × 7) is positively polarized because the natural Si(111)-(7 × 7) surface is composed of top positive Si nuclei and negative electrons making up the covalent bonds just below the surface Si nuclei and thus, overall, the Si(111)-(7 × 7) surface has a positive local dipole moment with a bias (offset) voltage of $-b$ ($= -0.6$ V). Thus, $P$ can be expressed as

$$P \propto a'(V + b)^5 + a''(V + b)^3 + a'''(V + b). \quad (4)$$

As the three voltages $V_{\rm dc}$, $V_{\rm ac}$, and $\tilde{V}$ are applied in superposition between the tip and sample in the SNDM experiment, the total applied voltage $V$ is expressed by

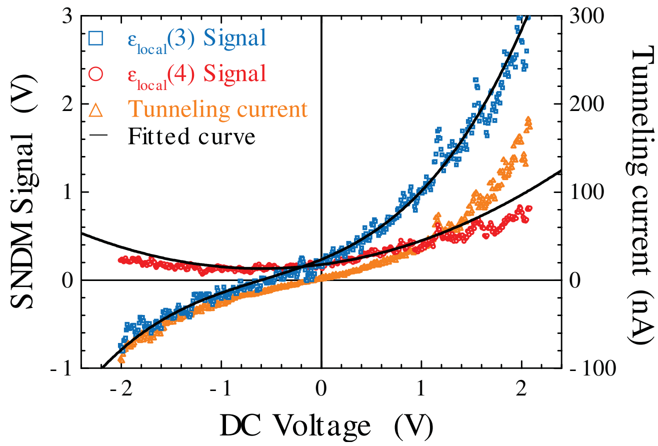


FIG. 4 (color). The dc-bias voltage dependences of the $\varepsilon_{\rm local}(3)$ signal, $\varepsilon_{\rm local}(4)$ signal, and tunneling current.

$$V = V_{\rm dc} + V_{\rm ac} + \tilde{V} \tag{5}$$

where $V_{\rm dc}$, $V_{\rm ac}$, and $\tilde{V}$ denote the dc-bias voltage, ac-bias voltage causing nonlinear dielectric response with relatively large amplitude and low frequency (in this case, 3 $V_{p\text{-}p}$ and 30 kHz), and small high-frequency voltage (typically 100 $mV_{p\text{-}p}$ at 2.2 GHz) for measuring the capacitance. This voltage application induces the dipole moment $P$ expressed by the equation

$$P = P_{\rm dc} + P_{\rm ac} + \tilde{P} \tag{6}$$

where $P_{\rm dc}$, $P_{\rm ac}$, and $\tilde{P}$ denote the dc, ac, and high-frequency components of the induced dipole moment, respectively.

By substituting Eqs. (5) and (6) into Eq. (4) and extracting the term connecting $\tilde{P}$ and $\tilde{V}$ only, which determines the actual measured capacitance detected by the SNDM microwave probe, we can obtain the relationship between the small high-frequency microwave voltage $\tilde{V}$ and the small high-frequency dipole moment $\tilde{P}$ induced by $\tilde{V}$ up to the second-order term of $V_{\rm ac}$:

$$\begin{aligned}\tilde{P} \propto &\{5a'((V_{\rm dc}+b)+V_{\rm ac})^4 \\ &+ 3a''((V_{\rm dc}+b)+V_{\rm ac})^2 + a'''\}\tilde{V} \\ = &\{(5a'(V_{\rm dc}+b)^4 + 3a''(V_{\rm dc}+b)^2 + a''') \\ &+ (20a'(V_{\rm dc}+b)^3 + +6a''(V_{\rm dc}+b))V_{\rm ac} \\ &+ (30a'(V_{\rm dc}+b)^2 + 3a'')V_{\rm ac}^2 + \text{h.o.t.}\cdots\}\tilde{V}\end{aligned} \tag{7}$$

When we apply an alternating voltage $V_{\rm ac} = V_p \cos\omega_p t$ to the specimen just under the tip, causing a nonlinear dielectric response, we finally obtain:

$$\frac{\tilde{P}(\omega_p)}{\tilde{V}} \propto (a(V_{\rm dc}+b)^3 + c(V_{\rm dc}+b))\cos\omega_p t, \tag{8}$$

$$\frac{\tilde{P}(2\omega_p)}{\tilde{V}} \propto \left(\frac{3}{4}a(V_{\rm dc}+b)^2 + \frac{c}{4}\right)V_p \cos 2\omega_p t, \tag{9}$$

where

$$a = 20a'V_p, \tag{10}$$

$$c = 6a''V_p, \tag{11}$$

In Eqs. (8) and (9), $\tilde{P}(\omega_p)/\tilde{V}$ and $\tilde{P}(2\omega_p)/\tilde{V}$ show the derivative (microwave) capacitance response varying with the frequency of the applied voltage $\omega_p$ and with the doubled frequency $2\omega_p$, respectively. Comparing Eq. (2) with Eqs. (8) and (9), we obtain the relative magnitudes of the $\varepsilon_{\rm local}(3)$ signal $V\varepsilon_{\rm local}(3)$ and $\varepsilon_{\rm local}(4)$ signal $V\varepsilon_{\rm local}(4)$ as functions of the dc-bias voltage $V_{\rm dc}$:

$$V\varepsilon_{\rm local}(3) = a(V_{\rm dc}+b)^3 + c(V_{\rm dc}+b), \tag{12}$$

$$V\varepsilon_{\rm local}(4) = \left(\frac{3}{4}a(V_{\rm dc}+b)^2 + \frac{c}{4}\right)V_p. \tag{13}$$

By fitting these equations to the measured curve in Fig. 4, we obtained the parameters $a = 0.11\ \mathrm{V}^{-2}$, $b = 0.6$ V and $c = 0.4$. Using these values, we also plotted Eqs. (12) and (13) in Fig. 4. The results, which show good agreement with the measured values, suggest that if we are to calculate the atomic polarization using the perturbation theory in quantum mechanics, at least a fifth order perturbation calculation is required.

In conclusion, this is the first successful demonstration of direct atomic dipole moment observation. Since the technique, used to detect dielectric properties and topography, is applicable not only to semiconductors but also both polar and nonpolar dielectric materials, it is expected that NC-SNDM will contribute to the study of electric dipole moment distribution in insulating materials at the atomic level.

*Corresponding author.
cho@riec.tohoku.ac.jp

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