How Humidity Affects on Scanning Nonlinear Dielectric Microscope*  

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The dopant type and carrier concentration in a patterned semiconductor sample with three different doping regions were measured by scanning nonlinear dielectric microscope (SNDM). SNDM is used in the way of a scanning capacitance microscopy (SCM) with a new detection mechanism based on frequency detection. The topographic, pn-distribution and the carrier concentration images of a patterned semiconductor sample were measured at the same time. In concurrence with a demonstration of the SNDM-SCM measurements, the influence of an adsorbed water layer on measurements is evaluated in the vacuum and in the air over a relative humidity (RH) range of 20 to 80%. Adverse affects on capacitance measurements due to the variation in RH are revealed.  
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I. INTRODUCTION

Scanning Nonlinear Dielectric Microscope (SNDM) is developed to measure the distribution of polarization in the ferroelectrics [1]. The change in the nonlinear dielectric constant is evaluated from the detection of the change in the frequency of electric inductance-capacitance oscillator. It figures out the remnant polarization distribution and crystallinity of the ferroelectrics. The quantitative analysis of the linear and nonlinear dielectric constants of the ferroelectric thin films is possible by SNDM [2]. The development of this method has continued until now, the nonlinear dielectric constant due to the sample surface (high-order nonlinear dielectric microscope) [3] is implemented, and the application of SNDM to the ferroelectric data storage has been demonstrated [4]. The effect of adsorbed water on the SNDM in ferroelectric materials also reported recently [5].

The evaluation of the conductive type and carrier concentration in semiconductor sample is carried out by various methods based on scanning tunneling microscope (STM) [6–8]. Patterned semiconductor devices will be common in the near future as objects. Regarding the practical use in the air, objects usually have an insulating oxide layer on the surface. The methods based on the atomic force microscope (AFM) are useful for the measurement in such case. Different doping areas in the semiconductor sample were resolved using the tapping (dynamic) mode AFM by the phase-imaging method, which is monitoring the phase difference in the cantilever oscillation with applying a direct current bias [9, 10]. AFM related methods such as Kelvin probe force microscope (KFM) [11–14] and scanning capacitance microscope (SCM) [15] are commonly used for the dopant measurements at present. In principle, scanning Maxwell-stress microscope (SMM) [16] and SNDM are also available to measure the capacitance (C) of the sample. When the SNDM is used for semiconductor samples, the conductive type and carrier concentration are measurable from the capacitance change of the semiconductor, which is corresponding to the change in the nonlinear dielectric constant of the ferroelectrics. Instead of using the RCA video-disc capacitance detector (signal: dC/dV) which is used in the conventional SCM, the difference in frequency is detected in the case of SNDM, hence, it is positioned as an SCM with a new detection sensor [1]. Compare to the conventional SCM method, the SNDM method has the advantages in the high sensitivity (∼10−22 F) and stable detection [17] due to some mechanical factors, such as the short path for the detection of radio frequency signal, frequency modulation and detection the phase shift. In this study, we measured the doping type and carrier concentration of a patterned Si sample using the SNDM and demonstrated the SNDM-SCM function as a new application. The humidity effects on the capacitive measurements by SNDM are also investigated to give an indication of the adsorbed-water effects on nano-order measurements by scanning probe microscope in the air.

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FIG. 1: Schematic drawings of a patterned doping sample. (a) A topographic image. Each square area (5 × 5 μm²) was patterned. (b) Apparent brightness based on a model of polarity image. The darkest (n-region) square is corresponds to the bright square in (a). (c) Apparent brightness based on a model of concentration image. Three different regions (p-, n- and n⁺-) are indicated in the drawing and filled by different colours for distinction.

II. EXPERIMENTAL

The experiments carried out by an environmental controlled scanning probe microscope unit (SPA-300HV, SII NanoTechnology) in the SNDM mode. Simultaneous AFM and SNDM measurements are possible in the vacuum (<~ 10⁻⁴ Torr) or in the humidity-controlled air [20-80% in relative humidity (RH), 1% in accuracy]. A topographic image of a square sample (Nicon) is shown in Fig. 1(a), each square area (5 × 5 μm²) was patterned; the p-area (B dope, 2 × 10¹⁶ atom/cm⁻³) and n⁺-area (As dope, 5 × 10¹⁹ atom/cm⁻³) were made on the n-type substrate (1 × 10¹⁵ atom/cm⁻³). Natural oxide layers exist on the sample surface.

III. RESULTS AND DISCUSSION

A. Application of SNDM for semiconductor surface as SCM

The resonant circuit in the detection system of SNDM is consisted of the capacitance, between the cantilever and the sample, and the inductance in the quasi-microwave oscillator. The oscillation frequency of the system (Fᵣ, 0.8-1.0 GHz) is decided from the inductance (L) and the capacitance of the total system.

\[ F_r = \frac{1}{2\pi} \sqrt{\frac{L}{C}}. \]  

(1)

Fr becomes lower according to the increase in C. Because the sample capacitance (Cₛ) is included in C, the change of sample capacitance (ΔCₛ) is detected as ΔFᵣ.

In the contact AFM mode, in which SNDM measurements are carried out, the junction of the conductive probe/surface oxide layer/semiconductor sample has the general MOS structure. When an electric field was applied to the junction by applying a voltage to the sample, free carriers in the semiconductor began to migrate. In the case of the charge polarity of the conductive probe is the same as that of the majority carrier in the sample; the depletion layer is formed in the semiconductor under the probe according to the strength of the electric field. The depth of depletion layer (W), which is corresponding to the distance between electrodes of a simple electrode system, is a determination factor of Cₛ. An alternative electric field with a frequency of Fₛ (several tens of kHz) introduces changes in the depletion layer in sync with Fₛ. As a result, Fᵣ is subject to Fₛ. The depth of the depletion layer from the semiconductor surface depends on the carrier concentration, it becomes deeper at the lower concentration. Depending on the carrier type (conduction electron/hole), the phase (θ) of the change in the depletion layer is reversal. Above mentioned features of the semiconductor carrier are obtainable by the synchronism detection of Fₛ with Fᵣ as a reference signal. Therefore, the planer mapping of the Fᵣ during scanning in the AFM mode makes possible the simultaneous measurement of the topographic, 2-dimentional distribution of carrier concentration and the carrier type images.

In the case of a native oxide/p-area is located just under the probe, the capacitance due to the native oxide layer (Cₒ) is detected when the sample is at a positive potential (Vₛ > 0). The total capacitance decreased due to the formation of a depletion layer at the negative sample potential (Vₛ < 0), as a result of the series connection of the capacitances of a native oxide layer and depletion layer (Cₛ). According to the expanse of the depletion layer at the higher electric potential, C decreases due to the decrease in Cₛ. In the case of a native oxide/n-area is located just under the probe, a depletion layer is formed when the sample is at a positive potential. The gradient of the capacitance is positive in the p-area and negative in the n-area. In our equipment, the image contrast is set as the positive gradient is displayed in bright tone; a p-area is shown brightly and an n-area is shown darkly in the image. Figure 1(b) shows an expected pn-distribution image in a square pattern [Fig. 1(a)], which is corresponding to the polarity image, as in the case of a ferroelectric sample.

An expected concentration image is shown in Fig. 1(c). In the case of the present sample, the carrier concentration is estimated almost same as the dopant concentration, n⁺-area > p-area > n-substrate. The synchronous component of the gradient with the applied AC voltage indicates the depth of depletion layer, because the depth depends on the carrier concentration. The depletion layer decreases in depth at larger impurity concentration, an area with lower dopant concentration is displayed brighter than a highly doped area. Namely, a p⁺-area is observed darker than a p-area and an n⁺-area is observed brighter than an n-area.
B. Humidity effects on SNDM measurements

At measurements of electric properties on semiconductor surfaces, it is well known that adsorbed water layers causes fudge factors, such as the poor reproducibility and leakage current. The evacuation, low humidity atmosphere and hydrophobic treatment are the effective ways to remove the adsorbed water layers. The actual effect of adsorbed water layers on the SNDM signal is examined under various humidity conditions. Figures 2 show \( pn \)-images [(a)-(g)] and concentration images [(h)-(n)] obtained at \( V_s = \pm 0.25 \text{ V} \) in the air, under the range of RH from 80 to 20%, and in the vacuum. The \( p \)-doped area is observed more distended and \( n \)-area is observed brightly at higher humidity conditions. Under the RH of 80%, square patterns \((p\text{-areas})\) in both images distended and border between the different areas were not sharp. Image contrast of \( p \) - and \( n \)-area in Fig. 2(a) was inversion. In Fig.2 (h), the huge difference between the concentrations of \( p \)- and \( n^+ \)-areas was hardly distinguishable. At an RH of 70%, the shape of \( p \)-areas was still distended and broad in Figs. 2(b) and (i). The image contrast changed significantly from the previous ones in both images, but they were still different from the expected images. The contrast of \( n \) - and \( n^+ \)-areas in Fig. 2(b) and that of \( p \)- and \( n \)-areas in Fig. 2(l) were inversion. As comparing \( pn \)-distribution and concentration images carefully, it is found that the shape distention reduced between RH of 60% [Figs. 2(c), (j)] and 50% [Figs. 2(d), (k)]. The contrast inversion was still observed even at a RH of 20% [Figs. 2(e), (l)]. In contrast, images measured in the vacuum show no contrast inversion. Figs. 2(f) and (m) were obtained immediately after the evacuation \((1 \times 10^{-3} \text{ Torr})\) by turbo molecular pump (TMP). The shape of \( p \)-areas was observed much clearly and the contrast of three areas in the \( pn \)-distribution image is the same as expected one. The contrast of \( p \) - and \( n \)-areas in the concentration image is still inversion, but that of \( n \) - and \( n^+ \)-areas got right. After further evacuation, the contrast in the concentration image is observed as expected at \( 5 \times 10^{-6} \text{ Torr} \) [Figs. 2(g), (n)]. The distribution of the electric field just under the probe is less concentrated by the adsorbed water [5]. The lateral resolution becomes poor at high RH. The probe contact condition strongly effects on the observed image because SNDM measurements were operated in contact mode. The difference in the shape is due to the expansion of the apparent curvature radius by the adsorbed water layer as with previous studies [8, 11, 13, 14].

These differences were quantified by plotting the intensities of SNDM signals at \( V_s = \pm 0.25 \text{ V} \). The \( pn \)-distribution signal [Fig. 3(a)] of \( p \)-area increased with RH until 60% and decreased at higher humidity. Decrement in intensity corresponds to the black out of \( p \)-area between RH of 60 and 70% as shown in Figs. 2(b) and (c). That of \( n \)-area show a negative value in vacuum (RH=0%) as theoretically expected, but came to positive value in the middle humidity range and increased again above a RH of 60%. The change in brightness of \( n \)-area in the \( pn \)-distribution images [Figs. 2(a)-(f)] agreed with this plot. The \( n^+ \)-signal in the \( pn \)-distribution kept negative values, slightly decreased from the expected value with increase in RH. The initial absolute value is smaller than that of \( n \)-area due to the narrower depletion layer as expected.

In the air environment, detected signals are regarded as sum of expected signal from the sample and unexpected effects of the large specific inductive capacity \((\varepsilon = 78.3 \text{ at room temperature})\). The equilibrium thickness of water layer, \( D \), on a Si surface in the air at \( T = 298 \text{ K} \) is calculated from a total free energy [18].

\[
D = \left( \frac{Av}{6\pi kT \ln(p/p_0)} \right)^{1/3}
\]

(2)
The thickness of the adsorbed water layer.

\[ \text{Thickness} = \frac{A}{k} \]

where \( A \) is the Hamaker constant of \(-1.0 \times 10^{-30} \) J for the Si-H2O-air interface and \( k \) is the Boltzmann constant. 

The ratio of the difference in SNDM signal intensities obtained at \( V_s = \pm 0.25 \) V. (a) \( p-n \)-distribution signal. (b) ratio of difference in \( p-n \)-distribution signal. (c) Calculated thickness of the adsorbed water layer.

FIG. 3: Relationship between the relative humidity and the SNDM signal intensities obtained at \( V_s = \pm 0.25 \) V. (a) \( p-n \)-distribution signal. (b) ratio of difference in \( p-n \)-distribution signal. (c) Calculated thickness of the adsorbed water layer.

where \( A \) is the Hamaker constant of \(-1.0 \times 10^{-30} \) J for the Si-H2O-air interface and \( k \) is the Boltzmann constant.

\[ v = \frac{M}{L}, M \text{ and } L \text{ are the molar weight and Avogadro number, respectively.} \]

Here, it is assumed that the density of water in the adsorbed layer, \( \rho \), is constant at any RH \((p/p_0)\). The thickness of water layer increases slowly and exceeds 0.2 nm at a RH of 60% as shown by the red line in Fig. 3(b). The calculated thickness well agrees with previous tribological studies [19, 20].

The ratio of \( n \) and \( p \)-signals to the initial value in the vacuum \((RH=\sim 0\%)\) gently increased along with the increment in the calculated thickness of adsorbed water layer [Fig. 3(b)]. Therefore it is indicated that the changes in SNDM signals are also caused by the adsorbed water.

In the case of \( n^+ \)-signal, the significant change occurred in above RH=60%. It is agreed well to the starting RH of surface ionic/current diffusion [21, 22]. Because of the amount of the carrier concentration in \( n^+ \)-area is about one thousandth of other areas, the effect of adsorbed water layer significantly appeared from the lower RH.

Next, the dependence of the SNDM signal, corresponding to \( dC/dV_s \), on the applied voltage is investigated. Measured \( dC/dV_s - V_s \) curves and integrated \( C - V_s \) curves in \( p \) and \( n \)-areas are shown in Fig. 4. \( V_s \) was varied from -2 to 2 V. In vacuum, one peak appeared in \( p \) and \( n \)-signal curves [Fig. 4(a)]. It means that the capacitance of the \( p \)-area (\( n \)-area) increases (decreases) with increment in voltage. In the air at low RH, the tendency of the detected signal and capacitance were same as it would in vacuum. But the peaks became narrower, its intensity became weaker and peak tops shifted to lower voltage [Fig. 4(b)]. At RH=40%, the deformation of the curves began and the peak tops shifted to the lower voltage again. The deformation of the curves became more significant at RH=60%, but the peak tops slightly slid back to the right direction.

The behaviour of \( dC/dV_s \) curves will be discussed in two parts, the deformation of the curves and peak shift. The possible origins of the deformation of the \( dC/dV_s - V_s \) and \( C - V_s \) curves are the formation of the inversion layer and the interfusion of the signals. At RH=40%, only the deformation of the \( n \)-curve is significant. The appearance of the inverse peak on the \( n \)-curve suggests the formation of the \( p \)-type inversion layer in the \( n \)-area induced by the adsorbed water ions. The intensity of the \( n \)-peak reverted at RH=60%, because the signal was detected through the inversion layer due to the increase of the depth sensitivity as same as the case of the SNDM measurements on LiTaO3 [5]. Additionally, the signal interfusion might carry over because the adsorbed water layer played the role of a common electrode, then the shape of the curves resembled each other in appearance. Using a geometrical calculation with well known values, such as the bond length between O-H (0.096 nm), atomic radius of H (0.03 nm), ionic radius of O (0.12 nm) and bond angle between H-O-H (104.5°), the estimated molecular occupied area does not exceed 0.05 nm². The water layer thickness of 0.2 nm at RH=60%, one molecule occupies 0.15 nm², as assuming that the spherical molecules are evenly spaced and lie flat on the surface. The distance between the water molecules is 0.46 nm (as reference, 0.38 nm in water liquid at RT) at RH=55%, where the surface ionic/current diffusion already started [21]. The large empty space surrounded an adsorbed water molecule at low RH, the distance is calculated as 0.49 and 0.53 nm at RH of 40 and 25%, respectively. The interaction between water molecules was very weak, so that the signal interfusion at low humidity was negligible.

The peak shift due to the RH change was clearly found in our experiment as shown in Fig. 4. The shift is caused by two origins; trapping charge in the SiO₂/Si interface and the effective voltage change due to the adsorbed water layer which is bridging between the probe and the sample. The former caused the entire shift to the left and the latter caused the peaks to get closer to each other. The entire shift of \( C - V_s \) curve is caused by the fixed trapped charge in the oxide layer and/or the SiO₂/Si interface trapped charge in the case of the general MOS diode. In our case, it is clear that the shape of the \( C - V_s \) curve was changed by the comparison of the Figs. 4(a) and (b). The shift amount increased with the increase in the voltage, and it is well known behaviour due to the interface trapped charge [23].

The adsorbed water with high dielectric constant causes the apparent distance to be smaller than the actual distance between the probe and the sample. From the definition of the capacitance, \( C = \varepsilon S/d \), the capacitance changes when adsorbed water exists on the surface. For example, if the gap between the probe and the sample is filled up with a material of duple dielectric constant, the capacitance become equal to the value with the half.
FIG. 4: The voltage dependence of the measured SNDM signal and capacitance. The capacitance was calculated by integration of the detected signal. Curves were measured (a) in vacuum \(1.3 \times 10^{-2}\) Torr, and in air (b) RH=25%, (c) RH=40%, (d) RH=60%.

The change in the apparent net distance between the probe and the sample caused the change of the effective applied voltage larger, and in consequence, the measured signal shifted to the centre with change in RH. By the comparison of Figs. 4(a) and (b), the shift of the \(C-V\) curve occurred even at the low humidity. The distance between the peaks of \(n\)- and \(p\)-curves decreased at higher humidity; 1.5 V in vacuum, then 1.3, 1.0 and 0.9 V at RH=25, 45 and 60%, respectively. Namely, the amount of the shift increased with the increase of the meniscus size.

IV. CONCLUSION

The variation of RH, namely, the variation in the amount of adsorbed water brings the inaccuracy and poor reproducibility into the SNDM measurements. Not only the surface ionic/current diffusion at high RH, other adverse affects for capacitance measurements became clear.
The adsorbed water layer formed the inversion layer and caused the deformation of the $C-V_s$ curve. It also raised the interfusion of the SNDM signals by playing a role of a common electrode at high RH. The high dielectric constant of water resulted in the unexpected shift of the SNDM signal peaks by a variance of the effective applied voltage. The interface trapped charge caused the entire shift of the $C-V_s$ curves. These adverse effects are common for the minute electric/capacitive measurements, irrespective of samples, by scanning probe microscopes in the air.

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