Si(111) Electrode/Electrolyte Interfacial Studied by \textit{in-situ} Second Harmonic Generation\(^{\dagger}\)

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Si(111) electrode has been widely used in electrochemical and photoelectrochemical studies. The potential dependent measurements of the second harmonic generation (SHG) were performed to study Si(111) electrode interface. At different azimuthal angles of the Si(111) and under different polarization combinations, the curve of the intensity of SHG with extern potential has a different form of line or parabola. Quantitative analysis showed that these differences in the potential-dependence can be explained by the isotropic and anisotropic contribution of the Si(111) electrode. The change in the isotropic and anisotropic contribution of the Si(111) electrode may be attributed to the increase in the doping concentration of Si(111) electrodes.

\textbf{Key words:} Second harmonic generation, Si(111) electrode/electrolyte, Doping density

\textbf{I. INTRODUCTION}

The solid-liquid interface not only has been a central issue in electrochemistry but also has an important application in heterogeneous catalysis, tribology, chemical sensors, and biofilm systems. The redox reactions in electrochemistry all occur on the electrode surface and the properties of the electrode surface play a decisive role in the electrochemical reaction.

Silicon has been the dominant material in semiconductor technology and is the intensively investigated electrode material in the field of electrochemistry and photoelectrochemistry. The interface structure of silicon is not only a fundamental subject to understand the electrochemical reaction mechanism, but also important to the application of silicon in solar cells, chips and materials.

In the past three decades, second harmonic generation (SHG) has been used to study the interface structure and dynamics of the electrode surface because of their surface/interface specificity and sensitivity. Up to now, SHG has been used to study ion adsorption [1–3], molecular orientation, and the modulation of molecular orientation of electrode/electrolyte by the applied potential at single-crystal and polycrystalline electrode interfaces [4–8]. In such studies on electrode/electrolyte interface, potential-dependent SHG measurement is an important method. It is widely used in the study of a metal oxide semiconductor (MOS), metal-semiconductor (MS) structure, and Si-SiO\(_2\) electrode/electrolyte interface. Also, the growth of gold particles on the silicon surface by SHG has been studied [9, 10]. How to explain the result of the potential-dependent SHG measurement has been a controversial issue. A semi-empirical model called the parabolic model has been used to describe this potential dependence. Recently, the semi-empirical model was demonstrated by group theory and explained the SHG signals of silicon and zinc blende as a function of applied potential [11]. However, whether the parabolic model is universal and whether the minimum point of the parabolic response corresponds to the flatband potential of a semiconductor electrode/electrolyte solution is still a focus question. In this work, we systematically studied the potential dependent SHG response from Si(111) electrode/electrolyte interface under pp, sp, 45° polarization combinations when the azimuthal angle of the Si(111) electrode was oriented at 0°, 30°, and 60°. Our results showed that the potential dependent SHG response was closely related to the polarization combinations and azimuthal angle. The increase in doping concentration may change the contribution of the isotropic and anisotropic Si(111) electrodes to the SHG, which results in different linear shapes of the potential-dependent SHG responses under different polarization combinations.

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II. EXPERIMENTS

A. Sample preparation

A home-built electrochemical cell consists of a Pt wire as the counter electrode, an Ag+/Ag (10 mmol/L AgNO$_3$ in acetonitrile solution) electrode as the reference electrode, and Teflon O-rings to prevent leakage of the cell. Before each experiment, the cell is cleaned with a 3:1 solution of H$_2$SO$_4$ and 30% H$_2$O$_2$, and rinsed thoroughly with Millipore water (18.2 MΩ-cm).

The working electrode is Si(111) wafer (Hefei Kejing Materials Technology Co., Ltd.), the resistivity of n-type arsenic-doped Si(111) wafer is 0.001–0.005 Ω-cm. Before the experiment, the Si(111) wafer was ultrasonically cleaned in acetone, ethanol and Millipore water (18.2 MΩ-cm) for 10 min and then rinsed with Millipore water and dried with ultrapure nitrogen gas. The Si(111) wafer is held to the cell by Ga-In conductive adhesive on the back of the silicon wafer and pressed against a fused quartz window. The electrode potential of the working electrode was regulated by a potentiostat (Princeton Applied Research, Model 263A). The solvent used in the experiment was acetonitrile (CH$_3$CN, HPLC purity, SIGMA) and contained 50 mmol/L supporting electrolyte of tetrabutylammonium tetrafluoroborate ([CH$_3$(CH$_2$)$_3$]$_4$NBF$_4$, J&K).

B. SHG setup

The reflected-geometry SHG setup has been described in detail previously [12, 13]. A broadband tunable mode-locked femtosecond Ti:Sapphire laser (Tsunami 3960C, Spectra-Physics) with high-repetition rate (82 MHz) and short-pulse width (80 fs) was used for measuring the SHG signal from the Si(111)/CH$_3$CN interface. The femtosecond laser can not only effectively reduce or avoid the damage of the laser thermal effect on the sample but also easily detect weak signals. The incident angle of 808 nm fundamental laser beam was 60° from the surface normal. The polarization of the 808 nm fundamental laser beam was controlled by a half-wave plate and the polarization of SHG signal was controlled by a polarizer. To optimize the SHG signal, the collimated fundamental laser beam was purified with a polarizer and a long-wavelength filter, and the SHG signal was purified with a short-wavelength pass filter and a monochromator. The SHG signal in the reflected direction was collected with a high-gain photomultiplier (R585, Hamamatsu) and a photon counter (SR400, Stanford).

C. Air/Si(111) interface SHG measurements

Before the measurement of the potential-dependent SHG, the rotational anisotropy of the Si(111) wafer was measured under ambient air. In this process, a computer was used to control the stepper motor and record the SHG intensity. The rotational anisotropy of the Si(111) wafer can be obtained by SHG intensity versus rotation angle simultaneously.

D. Potential dependent SHG measurements

The azimuthal angle [211] is defined as the angle between the direction of the Si(111) crystal surface and the projection of the incident light wave vector (FIG. 1). The three-fold symmetry of Si(111) still existed even the applied potential on the Si(111)/CH$_3$CN interface was varied [8]. Therefore, the azimuthal angle of the Si(111) wafer was fixed at 0°, 30° and 60° respectively in the electrochemical experiment. The applied potential was a linear scanning from 0 V to 1.5 V (vs. Ag/Ag$^+$ reference electrode) toward the negative potential. In all potential-dependent SHG measurement, the potential, the current, and the SHG signal were recorded simultaneously under different polarization combinations.

E. Theory

When a DC field is applied on the interface, the effective second-order polarization intensity can be described by [14]:

\[
I^{(2)}_{\text{eff}}(2\omega) = \chi^{(2)}_{\text{eff}} : E(\omega)E(\omega) + \chi^{(3)}_{\text{eff}} : E(\omega)E(\omega)E(\text{dc})
\]

where the third-order term refers to the potential-dependent part, E(dc) is the electrostatic field perpendicular to the interface, which mainly passes through the space charge region of the semiconductor. The electrostatic field strength depends on the depth of the space charge region, which is greatly affected by the doping density. If no chemical or physical changes occur on the electrochemical surface, to explain the potential-dependent changes in the SHG response, Eq.(1) can be...
rewritten in terms of the SHG intensity as [15]:

$$I_{\text{SHG}} \propto \left| \chi_{\text{eff}}^{(2)} e^{i\theta} + \chi_{\text{eff}}^{(3)} \Delta \Phi \right|^2$$

$$\propto \left| \chi_{\text{eff}}^{(2)} e^{i\theta} + \chi_{\text{eff}}^{(3)} (E - E_{fb}) \right|^2 \quad (2)$$

where $\chi_{\text{eff}}^{(2)}$ is the effective second order susceptibility from the bulk and interface responses. $\chi_{\text{eff}}^{(3)}$ is the effective third order susceptibility from charge induced third-order bulk response. $\theta$ is the relative phase of $\chi_{\text{eff}}^{(2)}$ and $\chi_{\text{eff}}^{(3)}$ [16]. The potential drop $\Delta \Phi$ of the semiconductor space charge layer is proportional to the difference between the applied potential $E$ and the flatband potential $E_{fb}$. When the third-order nonlinear term dominates, the observed potential-dependent SHG response curve should be parabolic with a minimum near the flat band potential. When the second-order nonlinear term of the surface or bulk phase is dominant, the minimum value of the parabola depending on the potential will deviate from the flat band potential.

III. RESULTS AND DISCUSSION

A. Rotation anisotropy of SHG measurements from the air/Si(111) interface

FIG. 2 shows the rotational anisotropy of SHG, SHG intensity vs. azimuthal angle, from the bare Si(111) surface under pp polarization combination (p polarization is defined as the direction of the electric field in the plane of incidence), which has three-fold ($C_{3v}$) symmetry (FIG 2(b)), consistent with a previous report [15]. The three-fold rotation anisotropy of SHG intensities can be described by [17, 18]

$$I_{pp}(2\omega) \propto \left| A_{pp} + B_{pp} e^{\Delta \Phi \cos(3\phi)} \right|^2 \quad (3)$$

The isotropic coefficient $A_{pp}$ is related to the response of polarized electrons from out-of-normal plane (the response with the z component), corresponding to non-zero independent tensor elements $\chi_{zzz}$, $\chi_{iii}$, $\chi_{iiz} (i=x, y)$ and isotropic bulk elements. The anisotropy coefficient $B_{pp}$ is related to the response of polarized electrons from in-normal plane, corresponding to non-zero independent tensor elements $\chi_{ixx}$ and anisotropic bulk elements. The relative phase $\Delta_{AB}$ of the $A_{pp}$ and $B_{pp}$ can be obtained by

$$\frac{B_{pp}}{A_{pp}} = \frac{|B_{pp}|}{A_{pp}} e^{\Delta_{AB}} \quad (4)$$

Therefore, the rotation anisotropy of SHG measurements from the air/Si(111) was the result of the interference between complex coefficient $A_{pp}$ and $B_{pp}$ (FIG. 2). The alternating appearance of large and small peaks in FIG. 2(a) was mainly the change in the relative phase change of $A_{pp}$ and $B_{pp}$. Through fitting the data of the FIG. 2 by Eqs.(3) and (4), we can obtain $|B_{pp}|/|A_{pp}|=1.0448$ and $\Delta_{AB}=33^\circ$. FIG. 2 also shows that the SHG signal reaches the maximum as $\phi=0^\circ$ and reaches the minimum as $\phi=60^\circ$ (FIG. 2(a)), which is the same as the previous research [19].

B. Electrochemical measurements of Si(111)/CH₃CN system

To prevent oxidation or polycrystallinity from cyclic voltammetry, we have to choose a potential range called the depletion region from the cyclic voltammetry before applying potential, where the Si(111)/CH₃CN system can be regarded as a capacitor that only has the charging process of the electrical double layer as applied potential changing [20]. The cyclic voltammetry in FIG. 3(a) showed that there was no oxidation-reduction reaction in the potential range from 0 V to −1.5 V. Therefore, in the following section, we choose this potential range to perform the measurements of the potential-dependent SHG.

To understand the potential dependent SHG response, we first obtained the flatband potential $E_{fb}$ of the Si(111)/CH₃CN system by the classical capacitance method. The classical capacitance method is based on the Mott-Schottky relation that can be expressed
The intercept and the doping density can be obtained from $E_{fb}$ (FIG. 3(b)). The electronic charge. The temperature, special capacitance, using Eq. (5). The experiment temperature was 298 K. From the CN system with a scan rate of 50 mV/s. (b) The Mott-Schottky diagram from the Si(111)/CH$_3$CN system measured at 1500 Hz. The red dots are the experimental data, and the red solid line is obtained by fitting using Eq.(5). The experiment temperature was 298 K.

Further, in terms of the electric field induced second harmonic generation (EFISH), we can explain the decrease in the SHG signal when the applied voltage was more negative than the $E_{fb}$ under 45°s and pp polarization combinations were similar (FIG. 4(c, i)). Both of them firstly decreased monotonously in the potential range from 0 to −0.6 V and then tended to be horizontal in the potential range from −0.6 V to −1.5 V. However, under sp polarization combination, the SHG signal was invariable in the whole applied potential range (FIG. 4(f)). These differences in potential-dependent SHG responses under different polarization combinations between $\phi=30^\circ$ and $\phi=0^\circ$ indicated that the anisotropy contribution of the interface and bulk resulted in the different potential dependent SHG response.

When the azimuthal angle of the Si(111) electrode was $\phi=60^\circ$, the potential-dependent SHG under 45°s and pp polarization combinations were similar (FIG. 4(c, i)). Both of them firstly decreased monotonously in the potential range from 0 to −0.6 V and then tended to be horizontal in the potential range from −0.6 V to −1.5 V. However, under sp polarization combination, the SHG signal was invariable in the whole applied potential range (FIG. 4(f)). These differences in potential-dependent SHG can be also attributed by the different anisotropic contributions of different azimuthal angles of Si(111) electrode to the SHG. As it is shown in FIG. 4.

When the azimuthal angle of Si(111) electrode was $\phi=30^\circ$, the potential-dependent SHG response showed almost the same curve shape under pp, 45°s and sp polarization combinations. The SHG intensities of three curves decreased by 50 without minimum in the whole potential range (FIG. 4(b, e, h)). When the azimuthal angle of Si(111) electrode was $\phi=0^\circ$, the potential dependent SHG response showed three different curves (FIG. 4(a, d, g)). Under 45°s polarization combination, the SHG signal was almost constant; under sp polarization combination, the SHG signal decreased monotonously; under pp polarization combination, the SHG signal quickly raised to the maximum value and then remained unchanged from the range of 0 V to −0.2 V, the SHG signal decreased monotonously from the range of −0.2 V to −1.0 V, then the SHG signal was almost the same from −1.0 V to −1.5 V. The SHG signal under pp polarization combination at the azimuthal angle of $0^\circ$ was larger than the azimuthal angle of $30^\circ$, which suggested the anisotropy contribution of the interface and bulk was larger than that at the azimuthal angle of $0^\circ$. The difference in potential-dependent SHG responses under different polarization combinations between $\phi=30^\circ$ and $\phi=0^\circ$ indicated that the anisotropy contribution of the interface and bulk resulted in the different potential dependent SHG response.

C. Potential dependent SHG response of Si(111)/CH$_3$CN system

It has been reported that when the azimuthal angle of Si(111) electrode was $0^\circ$ and $60^\circ$, the SHG signal under pp polarization combination arises from both the isotropic and anisotropy contribution of the interface and bulk [15]. Eq.(3) predicts that the SHG signal under pp polarization combination arises only from the isotropic contribution of Si(111) electrode when the azimuthal angle of Si(111) electrode was $30^\circ$. In order to get the full understanding of the isotropic and anisotropy contribution, we did the potential-dependent SHG experiments when the azimuthal angles of Si(111) electrode were $0^\circ$, $30^\circ$ and $60^\circ$, as it is shown in FIG. 4.

As [15, 20]:

$$C_s^{-2} = \frac{2}{\varepsilon_0\varepsilon_A A_s^2} \left( E - E_{fb} - \frac{k_BT}{q} \right)$$

(5)

where $k_B$ is Boltzmann’s constant, $C_s$ is the interfacial capacitance, $A_s$ is electrode area, $T$ is the absolute temperature, $N_d$ is the doping density, and $q$ is the electronic charge. The $E_{fb}$ can be obtained from the $x$-axis intercept and the doping density can be obtained from the slope. Only the potential range between 0 V and $-0.8$ V can be fitted with the Mott-Schottky relation (FIG. 3(b)). The $E_{fb}$ was $-0.788$ V and the doping density was $1.08 \times 10^{21}$ cm$^{-3}$ by the intercept and slope.

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pairs separation, and caused the holes to be driven to the electrode/electrolyte interface and the electrons to be driven into the bulk [23, 24]. The presence of surface holes would reduce the concentration of electrons at the interface, which led to electron depletion (depletion region). In addition, the presence of holes also led to a decline in the DC field. When the applied potential was more negative than $E_{fb}$, there was an excess of electrons (accumulation area) at the semiconductor interface. The strong potential dependent SHG response only occurred in the depletion region, which indicates that electrons were not the source of the surface second harmonic response. Therefore, the electrostatic field generated in the depletion region of the space charge layer may polarize the Si(111) lattice and cause a strong SHG response, which is called EFISH. According to Eq.(2), the SHG intensity is proportional to the square of the potential drop $\Delta \phi$ of the space charge layer. When the applied potential was closer to $E_{fb}$, $\Delta \phi$ became smaller and the SHG intensity decreased. In the accumulation region, most carriers mainly existed on the surface, which can make Si(111) electrode like a metallic electrode. The potential drop in accumulation region occurs only in the range of a few angstroms, so the interface electric field has little effect on the polarization of the Si(111) lattice, which hardly cause a strong EFISH response in accumulation region.

D. The doping density of Si(111) electrode

As shown in FIG. 4(c, i), the potential dependent SHG curves are asymmetric. Only at the azimuthal angle of Si(111) electrode of 60°, the SHG curves showed the approximately traditional parabolic model under the 45°’s and pp polarization combinations. The results were partially similar to the previous study that showed non-parabolic potential dependence of SHG response from the same systems [15]. In addition, FIG. 4(b, e, h) showed that the trends of the potential-dependent SHG at different polarization combinations were also the same when the azimuthal angle of Si(111) electrode was $\phi=30^\circ$. However, in comparison with the previous work [15], there is no minimum of the SHG intensity near the $E_{fb}$ and SHG intensity did not increase when the applied potential was more negative than the $E_{fb}$ in our study, which only have decreased differently. Closely inspecting these result, we attributed the difference in the potential-dependent SHG at Si(111)/CH$_3$CN interface. The correlation between the SHG intensity and the doping concentration was more complicated, rather than a simple linear relation [25]. Mitchell et al. found that the potential-dependent SHG intensity was independent of the doping type and density for low-doped Si electrode ($\rho=2–120$ Ω·cm), instead, the SHG intensity strongly depends on heavily doped Si electrode ($\rho=0.002$ Ω·cm) [17]. Therefore, the doping density of Si(111) electrode leads to the different potential-dependent SHG response. Herein, the sample we used was doped with arsenic (As) ($N_d=1.08\times10^{21}$ cm$^{-3}$) as we discussed in Section III(B), and the sample used in the previous study was doped with phosphorus (P)
As a result, the two samples should have different interface properties, such as isotropy and anisotropy of Si(111) electrode, resulting in different behavior of the potential-dependent SHG.

Aktsipetrov et al. suggested that the minimum of potential-dependent SHG response represented the \( E_{\text{fb}} \) of Si and Ge electrodes in an aqueous electrolyte [8]. However, Richmond et al. subsequently pointed out that the minimum of potential dependent SHG response deviated from the \( E_{\text{fb}} \) due to the anisotropy and isotropy contribution of the Si electrode interface [6]. As discussed above, the variation in doping density of Si(111) electrode can lead to changes in anisotropy and isotropy of interface and further bring about the different potential-dependent SHG response in FIG. 4 from the previous study.

### E. Quantitative analysis for Si(111)/CH\(_3\)CN system

To understand the different potential-dependent SHG response in FIG. 4, we estimated the values of \( \chi^{(2)} \), \( \chi^{(3)} \), and the relative phase \( \theta \) from the fitting of the FIG. 4 by Eq.(2). As shown in Table I, the \( \chi^{(2)} \) was larger than \( \chi^{(3)} \) when azimuthal angle of Si(111) electrode was 30°. The potential-dependent SHG response showed almost the same curve shape under pp, 45°s and sp polarization combinations. This indicates that the anisotropy contribution of the interface and bulk to the signal is negligible under the 45°s and sp polarization combinations. Since the potential dependent SHG response is a typical parabolic shape only when \( \chi^{(3)} \) is dominant, the potential dependent response curve is not a parabolic shape when azimuthal angle of Si(111) electrode is 30°.

However, when the azimuthal angle of Si(111) electrode was 0°, the \( \chi^{(2)} \) and \( \chi^{(3, \text{eff}} \) cannot be accurately determined by fitting curve using Eq.(2), which indicates that both \( \chi^{(2)} \) and \( \chi^{(3)} \) contribute to the SHG response. Therefore, the data should be fitted with Eq.(6) [26]:

\[
I(2\omega) = |\chi^{(2)} + \chi^{(3)}]E_{\text{DC}}|^2 I(\omega)
\]

where \( I(2\omega) \) and \( I(\omega) \) are SHG and fundamental laser beam intensity, respectively. \( E_{\text{DC}} \) is the DC electric field at the interface. \( \chi^{(2)} \) is the second order nonlinear susceptibility tensors and \( \chi^{(3)} \) is the third order nonlinear susceptibility tensors. The \( \chi^{(2)} \) was dominant under the whole polarization combinations (Table II). From the fitting, three different sets of \( \chi^{(2)} \) and \( \chi^{(3)} \) values are shown in Table II. By analyzing the data, we found that the SHG signal remained almost unchanged at both from 0 V to \(-0.2 \) V and from \(-1.0 \) V to \(-1.5 \) V. In the range of 0 V to \(-0.2 \) V, the difference between \( \chi^{(2)} \) and \( \chi^{(3)} \) was larger than that in the range of \(-1.0 \) V to \(-1.5 \) V. The reason is that the Si(111) electrode generated e/h pairs when the electrode was irradiated with 808 nm beam. Under pp polarization combination, the Si(111) electrode interface accumulated holes, which resulted in the increase in the SHG signal at the range from 0 V to \(-0.2 \) V. When the applied potential became negative, the holes decreased because of the combination with electrons. The holes accumulated in Si(111) electrode interface would reduce the DC electric field. Therefore, the potential-dependent SHG signal decreased at the range from \(-0.2 \) V to \(-1.0 \) V. When the applied potential was from \(-1.0 \) V to \(-1.5 \) V, the Si(111) electrode interface accumulated more electrons, which could make Si(111) electrode more like a metallic electrode. Therefore, the potential-dependent SHG signal remained almost unchanged. The relative phase \( \theta \) cannot be obtained by Eq.(6).

When the azimuthal angle of Si(111) electrode was 60°, the \( \chi^{(2)} \) was dominant under the 45°s and pp polarization combinations. In contrast, the \( \chi^{(2)} \) was dominant under the sp polarization combinations (Table III). Therefore, under the 45°s and pp polarization combinations, the potential dependent SHG response has the same shape and differs from that of the sp polarization combination. As such, we have explained the different shapes of potential-dependent SHG response under different azimuthal angles and polarization combinations in terms of the anisotropy and isotropy contribution of

### Table I Fitting results of potential dependent SHG response for different polarization combinations at \( \phi=30^\circ \).

<table>
<thead>
<tr>
<th>Polarization combination</th>
<th>( \chi^{(2, \text{eff}} )</th>
<th>( \chi^{(3, \text{eff}} )</th>
<th>( \theta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>45°s</td>
<td>7.79±0.03</td>
<td>5.01±0.21</td>
<td>-9.80±1.02</td>
</tr>
<tr>
<td>sp</td>
<td>8.91±0.03</td>
<td>5.60±0.23</td>
<td>-12.80±0.99</td>
</tr>
<tr>
<td>pp</td>
<td>9.43±0.04</td>
<td>1.65±0.91</td>
<td>-13.05±0.97</td>
</tr>
</tbody>
</table>

### Table II Fitting results of potential dependent SHG response for different polarization combinations at \( \phi=0^\circ \). The relative phase \( \theta \) cannot be obtained by Eq.(6), and the values are not shown in the table.

<table>
<thead>
<tr>
<th>Polarization combination</th>
<th>( \chi^{(2, \text{eff}} )</th>
<th>( \chi^{(3, \text{eff}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>45°s</td>
<td>7.94±0.04</td>
<td>0.65±0.04</td>
</tr>
<tr>
<td>sp</td>
<td>14.70±0.04</td>
<td>2.93±0.05</td>
</tr>
<tr>
<td>pp (from 0 to (-0.2 ) V)</td>
<td>47.95±0.19</td>
<td>-1.50±1.21</td>
</tr>
<tr>
<td>pp (from (-0.2 ) V to (-1.0 ) V)</td>
<td>54.70±0.10</td>
<td>29.26±0.18</td>
</tr>
<tr>
<td>pp (from (-1.0 ) V to (-1.5 ) V)</td>
<td>-30.36±0.29</td>
<td>-4.48±0.23</td>
</tr>
</tbody>
</table>

### Table III Fitting results of potential dependent SHG response for different polarization combinations at \( \phi=60^\circ \).

<table>
<thead>
<tr>
<th>Polarization combination</th>
<th>( \chi^{(2, \text{eff}} )</th>
<th>( \chi^{(3, \text{eff}} )</th>
<th>( \theta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>45°s</td>
<td>9.49±0.06</td>
<td>15.60±0.14</td>
<td>60.79±0.44</td>
</tr>
<tr>
<td>sp</td>
<td>4.82±0.03</td>
<td>0.96±0.03</td>
<td>82.05±5.55</td>
</tr>
<tr>
<td>pp</td>
<td>7.28±0.04</td>
<td>11.25±0.11</td>
<td>51.16±0.60</td>
</tr>
</tbody>
</table>
the interface.

The microscopic molecular structure at the interface can be derived by microscopic susceptibility tensor elements under systematic polarization measurements for electrode/electrolyte interface. Our results here suggest that quantitative analysis for Si(111) electrode/electrolyte interface may be capable to interpret microscopic mechanism of potential dependent SHG response by systematic polarization measurements. Previous researches have demonstrated that quantitative and systematic polarization analysis was a powerful approach to study liquid interfaces [27, 28]. However, systematic polarization measurements have been uncommon for complicated electrochemical interfaces. This finding expends the quantitatively systematic polarization measurements in the liquid interfaces to the complicated electrochemical interfaces, which is important to study the mechanism of the electrode reaction.

IV. CONCLUSION

The potential-dependent SHG response of Si(111)/CH$_3$CN system was studied under the polarization combinations and at the azimuthal angle of 0°, 30° and 60°, respectively. The results have shown that the curve of this response was closely related to the polarization combinations and azimuthal angle, which implies that isotropic and anisotropic contributions of the interface to the SHG are different under such conditions. The changes in isotropic and anisotropic contributions of Si(111)/CH$_3$CN interface may be accounted for the doping density of Si(111) electrode. Moreover, quantitative analysis can be made to interpret this microscopic mechanism of potential-dependent SHG response. These findings indicate that the doping density of Si(111) electrode plays a significant role in interface structure and properties of Si(111) electrode/electrolyte. Such systematic polarization measurements can provide a new sight into the potential-dependent SHG response for complicated electrochemical interfaces.

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