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In situ second harmonic generation studies from covered Ag(111) electrodes

Abstract The second harmonic response of Ag(111) electrodes has been studied in the presence of adsorbates. Two different kind of systems have been investigated: films of biphenyl derivatives and halide adsorbates. The presence of the adsorbates is shown to affect markedly the isotropic response of the interface, while the aniso-tropic part seems to be generated solely by the metal.

Keywords Adsorbates · Biphenyl thiols · Halides · Second harmonic generation · Silver electrodes

Introduction

Second harmonic generation (SHG) is a well-known nonlinear phenomenon, and its application to the characterization of electrochemical interfaces has been the subject of numerous publications [1, 2, 3]. When light coming from a high-power laser impinges on the interphase between two centrosymmetric materials, be-cause of the strong interaction between the surface electrons and the electrical field of the electromagnetic wave, beside the reflected beam at the fundamental fre-quency, light at twice the frequency of the incident beam is also generated. The induced second harmonic current at the surface consists of contributions normal and parallel to the electrode surface. The specificity to the interfacial region, which is assured by the selection rules for centrosymmetric media, makes this technique attractive for the characterization of adsorption pro-cesses. Although the analysis of the second harmonic response is a complicated task, a systematic treatment of the measurements can provide interesting information about the electronic properties of the interface.

The application of this technique to electrochemical systems allows several parameters to be varied. The most important are: the electrode potential, the polar and azimuthal angles of incidence, and the polarization of the incident and the outgoing beams. The polarization can be either normal to the plane of incidence (*s* polar-ization), parallel (*p* polarization), or a combination of the two. The application of a potential difference to the interface alters the distribution of the surface electrons. In particular, the second harmonic response with normal polarization is quite sensitive to these changes.

Rotation of the electrode about an axis perpendicular to the surface gives the response as a function of the azimuthal angle. The signal reflects the symmetry of the surface and can be split into an isotropic and an aniso-tropic contribution. An adequate combination of the directions of polarization for the incident and the gen-erated second harmonic beams allows the determination of the different elements of the second-order suscepti-bility tensor [4].

In this contribution, we report the application of surface SHG measurements to various electrochemical interphases. A comparative analysis between the response of bare metallic surfaces and those covered by different adsorbates is undertaken.

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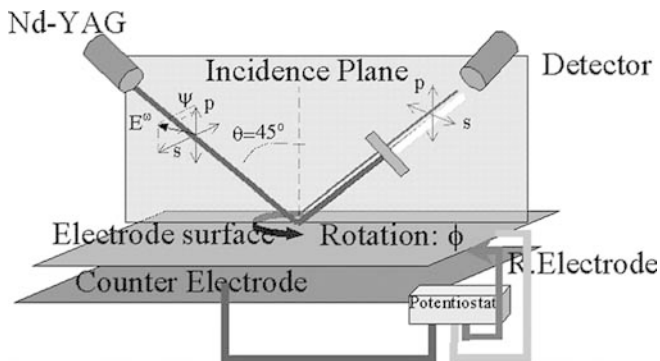89069 Ulm, Germany

Experimental

The experimental SHG set-up is summarized in Fig. 1. The exci-tation source was a Q-switched Nd:YAG laser with a beam light at 1064 nm, a pulse duration of 9 ns at a frequency of 20 Hz, and an energy of 250 mJ/cm^2 per pulse. The polar angle of incidence θ was

Fig. 1 Experimental set-up (schematic)

45°. The direction of polarization of both the fundamental and second harmonic beams was changed between $\psi = 0°$ ("p") and $\psi = 90°$ ("s"). The silver single-crystal electrode [(111) face] was rotated (polar angle ϕ) around an axis perpendicular to the surface and the SHG signal was recorded at different potential values (E_{SCE}) The reference electrode was a saturated calomel electrode (SCE). The sample preparation was explained in previous papers [5, 6].

Results and discussion

As mentioned in the Introduction, the intensity of the second harmonic signal generated at the interphase has an isotropic and an anisotropic contribution:

$$I_{SHG} = I_{iso} + I_{anis} \qquad (1)$$

The (111) orientation belongs to the C_{3v} group. According to the phenomenological treatment of Sipe et al. [7], the SHG signal intensities $I^{input,output}$, where the superscripts refer to the polarization of the incident (input) and second harmonic (output) light fields, have the following forms:

$$I_{SHG}^{pp} = |A_{iso}|^2 + |C_{anis}|^2 \cos^2(3\phi) \\ + 2|A_{iso}||C_{anis}| \cos(3\phi) \cos(\psi_{\tilde{A}\tilde{C}}) \qquad (2)$$

$$I_{SHG}^{ss} = |B_{anis}|^2 \sin^2(3\phi) \qquad (3)$$

$$I_{SHG}^{sp} = |\tilde{A}_{iso}|^2 + |\tilde{C}_{anis}|^2 \cos^2(3\phi) \\ + 2|\tilde{A}_{iso}||\tilde{C}_{anis}| \cos(3\phi) \cos(\psi_{\tilde{A}\tilde{C}}) \qquad (4)$$

The empirical parameters, A, B, and C contain, besides the Fresnel coefficients, different elements of the second-order susceptibility tensor, $\chi^{2\omega}$: A_{iso} (χ_{zxx}, χ_{xxz}, χ_{zzz}); $\tilde{A}_{iso}$ (χ_{zxx}); $C_{anis}(\chi_{xxx})$; $B_{anis}(\chi_{xxx})$; and $\tilde{C}_{anis}(\chi_{xxx})$. Because these empirical parameters are complex quantities, there are phase differences ψ_{ij} between them.

The response of a bare metal can be analyzed in the frame of a combination of the jellium model and density-functional theory [8, 9]. When an adsorbed layer is present at the interphase, resonances with electronic transitions may occur and must be taken into account. In this case the second-order susceptibility tensor can be considered as a sum of three different contributions [5]:

$$\chi_{Tot}^{2\omega} = \chi_m^{2\omega} + \Delta\chi_i^{2\omega} + \chi_{ads}^{2\omega} \qquad (5)$$

where $\chi_m^{2\omega}$ gives the response of the bare metal in absence of any adlayer, $\Delta\chi_i^{2\omega}$ is the perturbation to the metallic nonlinear polarizability by the presence of an adsorbate, and $\chi_{ads}^{2\omega}$ is the inherent contribution from the adsorbed film. The latter is determined by the individual susceptibilities β of the "N" adsorbed species and their relative orientations:

$$\chi_{ads}^{2\omega} = \sum_{i=1}^{N} <F> \beta_i \qquad (6)$$

where $<F>$ is the species distribution function for the adsorbates at the surface.

Figure 2 shows as an example the SHG signal for "ss", "pp" and "sp" directions of polarization as a function of the azimuthal angle ϕ at a constant potential value of -0.5 V. The film was obtained by adsorption of 4,4′-thiobis(benzenethiol). The three or six peaks for I_{SHG} as a function of the rotation angle ϕ reflect in all the cases the C_{3v} symmetry of the substrate and the signal can be described by Eqs. 3, 4, 5. The main contribution to the second harmonic response is obtained with the "pp" directions of polarization, and we focus in this case on the analysis of our results.

Figure 3, Fig. 4, and Fig. 5 represent the second harmonic response for the "pp" combination of the direction of polarization for different electrochemical interphases. The 3D plots show the dependence of the second harmonic response with the applied potential and the azimuthal rotation angle. Figure 3 corresponds to the response of a bare surface of Ag(111). Figure 4 and Fig. 5 show the results obtained with a Ag(111) surface covered by different adsorbates. The influence of the specific adsorption of anions on the SHG response can be examined in Fig. 4. On the other hand, films derivatized from thiols with different chemical
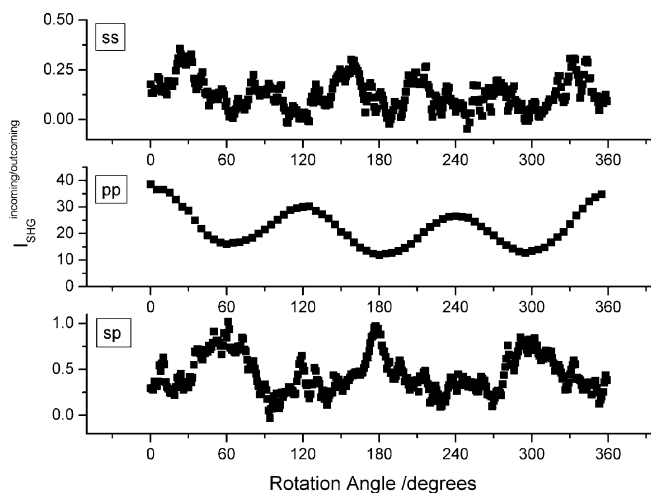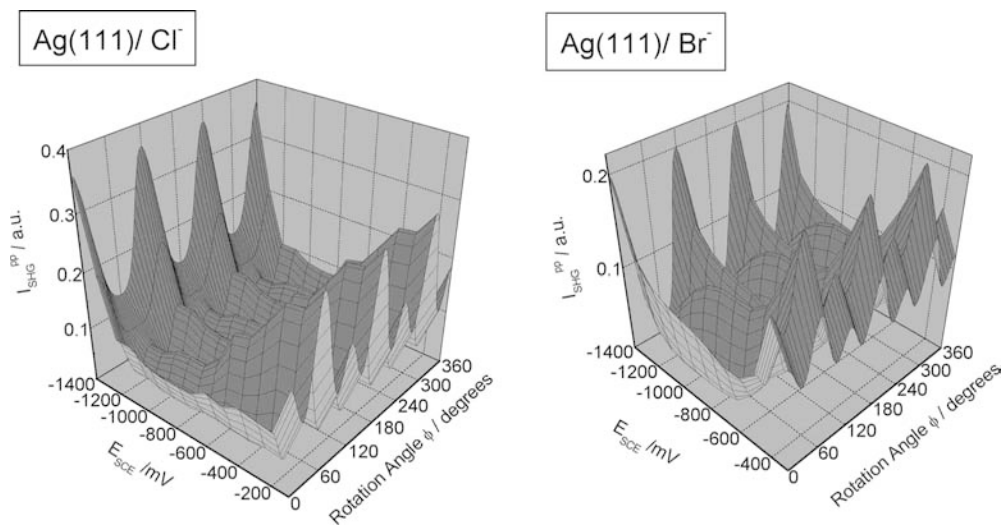

Fig. 2 Second harmonic response of a Ag(111) electrode covered with a film of 4,4′-thiobis(benzenethiol) for various polarizations; the electrode potential was set at -0.5 V
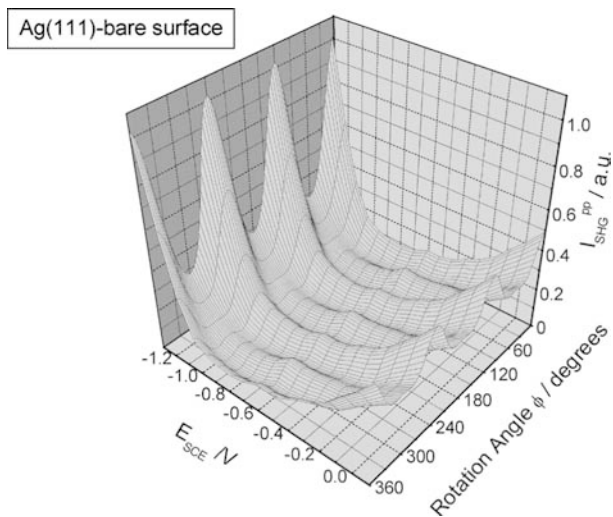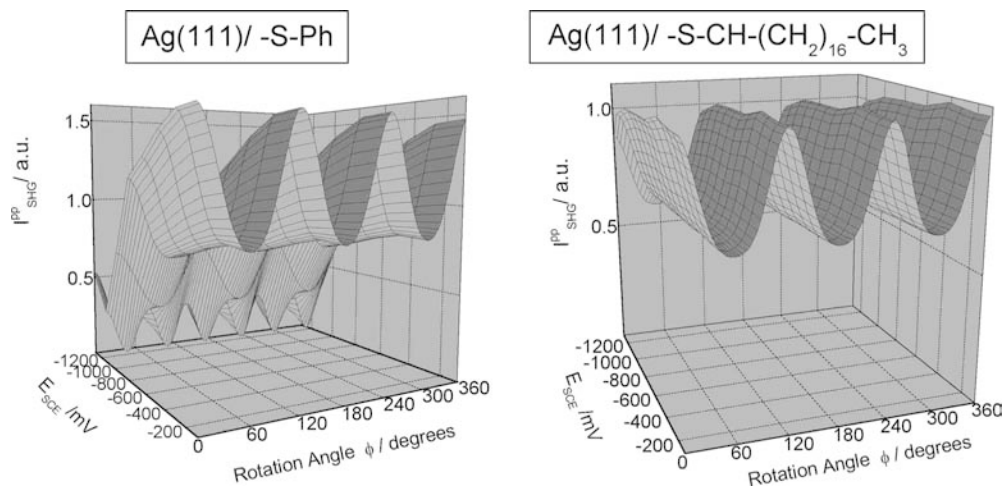
Fig. 3 Second harmonic response of a bare Ag(111) surface in the *p*-in *p*-out configuration; the electrolyte was an aqueous 50 mM KClO$_4$ solution
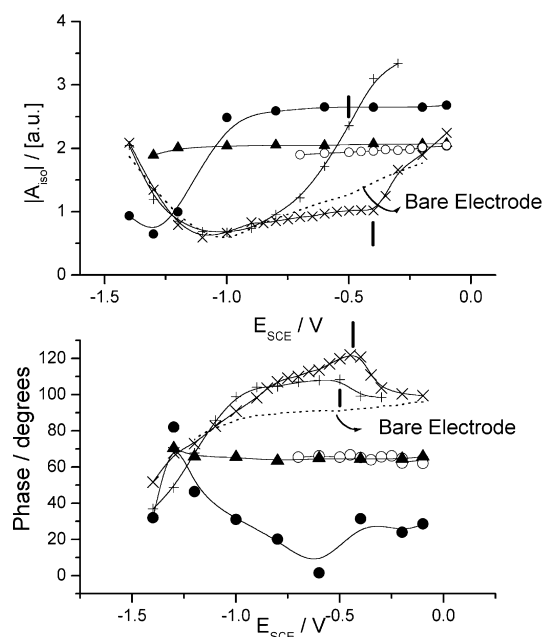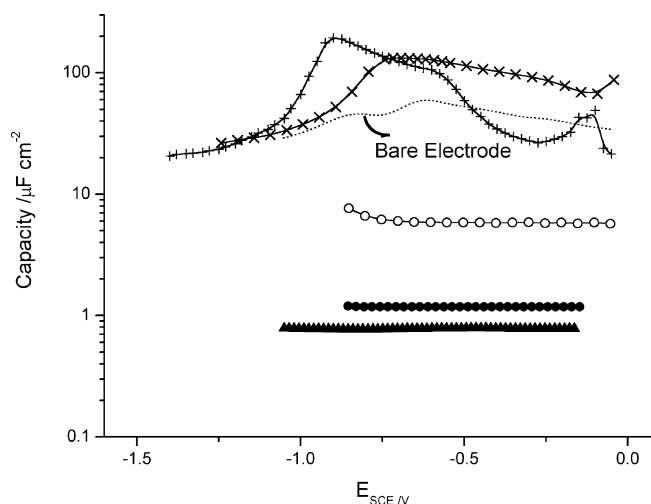
environments exhibit the behavior shown in Fig. 5. The three interphases give features for the I_{SHG} as a function of the rotation angle ϕ, which reflect in all the cases the C_{3v} symmetry of the substrate. However, this fact alone does not mean necessarily that the second harmonic signal comes exclusively from the Ag(111) surface, since usually the adsorbates form commensurate structures. The three interphases present a markedly different dependence of the second harmonic signal with the potential applied. In order to perform a more exhaustive analysis, the empirical parameters A_{iso}, C_{anis} and ψ_{AC} were calculated by fitting the experimental data with Eq. 3. While no significant changes are observed in the anisotropic parameter C_{anis}, the dependence of A_{iso} and ψ_{AC} with the applied potential and the nature of the adsorbate shows important differences. The results for A_{iso} and ψ_{AC} are shown in Fig. 6. The parameter C_{anis} contains the element χ_{xxx} of the susceptibility tensor corresponding to the current parallel to the surface. The invariance of this parameter indicates that the

Fig. 4 Second harmonic response of a Ag(111) electrode in a solution of 49 mM KClO$_4$ + 1 mM KCl (*left*) and in 49 mM KClO$_4$ + 1 mM KBr (*right*)

Fig. 5 Second harmonic response of a Ag(111) electrode covered by films derivatized from different thiols

Fig. 6 Isotropic amplitude and phase angle as a function of electrode potential for various systems. The symbols refer to the following systems: *crosses*, with Cl⁻ ions; *plus signs*, with Br⁻ ions; *filled circles*, HS-C₆H₄-S-C₆H₄-SH; *filled triangles*: octadecanethiol; *open circles*: benzenethiol. The *vertical lines* indicate phase transitions in adsorbed halide layers

anisotropic contribution is generated by the Ag(111) substrate. The parameter A_{iso} contains the elements χ_{zxx}, χ_{xzx}, and χ_{zzz} of the susceptibility tensor corresponding mainly to the current perpendicular to the surface. The applied potential, which produces an extra continuous electrical field also perpendicular to the surface, affects markedly these elements. In this case, it is difficult to decide if the differences observed relative to the bare surface are produced by the second, the third, or a combination of both terms of Eq. 5.

Figure 7 shows the capacitive curves for the different adlayers obtained superimposing an alternating signal of 10 mV amplitude and 10 Hz to a potential sweep of 10 mV/s. In some cases there is correlation between the changes observed in the capacitance and the isotropic parameter A_{iso} with the applied potential. This is particularly clear in the response of the interphase with adsorbed thiols, where a constancy of the A_{iso} parameter and the capacitance over the whole potential range of stability of the films are observed. The decrease at more negative potential values of A_{iso} for the film derivatized from the benzenethiol is due to a partial destruction of the film by a reductive process [5]. In the case of the specific adsorption of anions, the transition phases between different structures [10, 11, 12] are observed in both the capacitive and in the second harmonic responses. The relative phase between A_{iso} and C_{anis} also gives important information. While in the case of the adsorbates obtained from thiols the values of ψ_{AC} are lower than those observed for the bare surface of Ag(111), those corresponding to the adsorbed anions are

some higher. The values of ψ_{AC} lower than 90° indicate an absorption of the signal which could be caused by a resonance of the S–Ag bonding. Thiols with different chemical environments, such as a long hydrocarbon chain or an aromatic ring, give different responses.

Phase transitions in the specific adsorbed anions are often indicated by a drop of ψ_{AC}. This matter will be discussed more fully elsewhere [13]; here, we indicate two features in Fig. 6. For the case of bromide adsorption, these correspond to the formation of a $(3^{1/2}\times3^{1/2})R30°$ layer, which has been established by STM data [10, 11, 12]. The feature for the adsorbed chloride ions is probably caused by the same transition, but here the STM data are less clear.

Fig. 7 Interfacial capacity as a function of the electrode potential. The symbols have the same meaning as in Fig. 6

Conclusions

The presence of the adlayers on the metal surface of Ag(111) single-crystal electrodes have complex effects on the different contributions of the SH response:

1. The observed anisotropic response comes only from the substrate and there is no appreciable perturbation of this term by the presence of the adlayers. Thus the induced second harmonic currents parallel to the electrode surface are not affected by the adsorbed species investigated in the present work.
2. The isotropic contribution, which reflects the induced SH current perpendicular to the electrode surface, is strongly affected by the presence of different adsorbates. The potential dependence of the isotropic parameter presents characteristic features for each adlayer.
3. The changes observed in ψ_{AC} for the various investigated thiols in comparison to bare surfaces could be explained through a resonance caused by the Ag–S chemical bond. Because these changes are particular for each compound, this chemical bond seems to be

affected by the molecular environment. It is also independent of the potential, indicating no change in the nature of the bond within the range of stability.

4. Phase transitions in the adlayers of anions affect strongly the SHG signal. Contrary to the independence of the ψ_{AC} vs. potential observed with thiols, a sudden decrease of ψ_{AC} is observed at potential values where phase transitions occur between disordered–ordered structures of anions.

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