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Resonance X-ray Scattering from Pt(111) Surfaces under Water*

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The resonance x-ray scattering from the unmodified, clean Pt(111) surface is compared to theoretically predicted scattering. Self-consistent real-space multiple-scattering approach is used to calculate the real and imaginary parts of the atomic platinum scattering factor. The experimentally observed near-edge fine structures of the surface-scattering and fluorescence intensities are well reproduced by the calculations. In addition, more details are presented on our previous study [Phys. Rev. Lett. 83, 552 (1999)] of electrochemically formed oxide monolayer on the Pt(111) surface.

1. INTRODUCTION

In our recent studies [1] we have shown that the technique of surface resonance x-ray scattering can be used to detect the surface atoms whose core-binding energies are shifted compared with that of bulk atoms. Although it is well known that the real part of the resonance scattering factor exhibits a near-edge fine structure, similarly to the imaginary part [2], the relatively large core-binding energy shift found in our work was easily determined by ignoring the fine structure present in the data. Nevertheless, the fine structure in the surface scattering data contains information that could be used to learn important details about the surface under investigation: for example, solid-state effects, chemical nature, and short-range local structure.

In particular, such information cannot be obtained in any other way for buried interfaces, and the development of a technique to extract this information is important for a wide variety of materials used in energy technologies where the active interfaces are often buried under electrolytes. However, this can only be accomplished if the fine structure present in the data is understood theoretically. For this reason, we will compare the currently available state-of-the-art computation of the platinum atomic form factor (including solid-state effects) with our data obtained from the clean, ideally terminated surface of Pt(111). In doing so, we demonstrate that the surface resonance scattering is one of the most accurate ways to determine the atomic form factors for solid-state compounds. The reason for this accuracy is that the depth sensitivity can be controlled in the surface scattering from a monolayer to many layers thereby the aberrations due to the absorption can be completely eliminated.

In this article, we will briefly review the x-ray resonance scattering process, discuss the depth sensitivity of surface x-ray scattering, compare the clean surface data with the theoretical calculations, and finally discuss the data taken from the surface after oxidation.

2. ELASTIC CHANNEL OF RESONANCE X-RAY SCATTERING PROCESS

Resonance x-ray scattering occurs when a beam of monochromatic x-rays (with a narrow but finite band-width) interacts with an atom near the resonance energy of a quantum state of the atom, both elastic and inelastic scattering occurs. In case of the inelastic channel, simply known as the x-ray fluorescence process, the resonance behaves as two independent processes: absorption of

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the x-ray and the subsequent re-emission. In this case, the photon energy is not conserved precisely because the second step of the fluorescence is only limited by the life-time width of the ground state. Since the re-emission of the photon takes place independent of the absorption process, the emitted photon does not "remember" its relative phase to the incident photon and remains incoherent. These photons, although their energy may be very close to incoming photon energies, will produce a smooth background only. In our measurements these photons are eliminated by subtracting the background measured at the foot of the scan across the surface scattering rod [3].

The true elastic channel of resonance scattering occurs when the absorption and immediate re-emission takes place as a single quantum step. In this case, the atom involved is undisturbed, the energy of the atom is undetermined, and, more importantly, the emitted radiation is coherent with the primary radiation. The emitted photon will have a phase delay determined by the imaginary part of the resonance scattering factor [4]. It is also evident that one cannot determine from *which atom* the observed photon scattered. Therefore, appropriate phase delays from every atom in the system must be taken into account and the calculation of the expected intensity must include a coherent sum of all the atoms present in the system. This coherent sum can also be described more elegantly, in terms of path integral formalism, by a theorem that the incident photon probes all the space (all the atoms) to find the optimum path for diffraction [5].

In reality, both channels exist but the inelastic channel dominates when the energy band of incoming photon is broader than the life time of the ground state, and the elastic channel dominates in the opposite case. Therefore, as the energy width of incoming x-rays is narrowed (for example, by changing x-ray optics) the intensity of fluorescence signal relative to the elastic signal decreases [6]. Once the inelastic channels are eliminated in our measurements by the background substraction, the polarization-conserving elastic scattering process can be described, within the dipole approximation, as [7]

$$
\begin{aligned}
f(\omega) &= \sum_I \frac{r_0 \left|(\mathbf{p}\cdot\epsilon)_{IA}\right|^2}{m\hbar} \left[-\frac{2}{\omega_{AI}^n} \right. \\
&\left. + \frac{1}{\omega_{AI}^n - \omega - i\frac{\Gamma_I}{2\hbar}} + \frac{1}{\omega_{AI}^n + \omega} \right] \qquad (1)
\end{aligned}
$$

where r_0 is the Thompson cross section of an unbound electron, $\hbar\omega_{AI}^n$ is the energy difference between the ground state (A) and an intermediate quantum state (I) of nth atom in the system, and Γ_I is the life-time broadening. The first term in the square bracket represents the Thompson scattering cross section (the transition matrix summed over all the intermediate states is unity), the second term represents the absorption/emission process, and the third therm represents the emission/absorption process.

By separating the sum into real and imaginary parts, we obtain the resonance scattering factor:

$$
\begin{aligned}
R_n &= \frac{r_0}{m_e\hbar} \sum_I \left|(\mathbf{p}\cdot\epsilon)_{IA}\right|^2 \\
&\times \left[\frac{2\omega^2(\omega_{AI}^n - \omega) - \left(\frac{\Gamma_I}{2\hbar}\right)^2 (\omega_{AI}^n + 2\omega)}{\omega_{AI}^n(\omega_{AI}^n + \omega)\left[(\omega_{AI}^n - \omega)^2 + \left(\frac{\Gamma_I}{2\hbar}\right)^2\right]} + \frac{i\frac{\Gamma_I}{2\hbar}}{\left[(\omega_{AI}^n - \omega)^2 + \left(\frac{\Gamma_I}{2\hbar}\right)^2\right]} \right] \qquad (2)
\end{aligned}
$$

Contrary to usual practice, we do not ignore Γ_I in the real part of the resonance scattering cross section. The real and imaginary parts are illustrated in Fig. 1 for $\hbar\omega_{AI}^n = 10\ keV$ and $\Gamma_I = 5\ eV$. Note that the calculation is carried out only for a single intermediate quantum state. The summation over all *available* intermediate states is necessary to obtain a single atom resonance cross section. Consequently, the resonance scattering reflects the empty density of state around the atom. Indeed, the near-edge fine structure present in the resonance scattering is dominated by the solid state effect; this will be tested by comparing our data to the calculation based on a recently developed computational scheme. Also note that $\hbar\omega_{AI}^n$ is the energy *difference* between the two states of the atom; consequently, there is an ambiguity in our measurements: for example, if the measured $\hbar\omega_{AI}^n$ *increases*, we do not know whether the ground state energy is decreasing or the intermediate state energy is increasing. However, there is an upper limit for the intermediate state because it will eventually reach the vacuum level when the the work function of the solid is exceeded. Therefore, the surface resonance scattering is sensitive not only to the core-bindining energy shift but also to the energy shift of the intermediate state. Both can be determined if the value of one of them is known or can be determined by some other means.

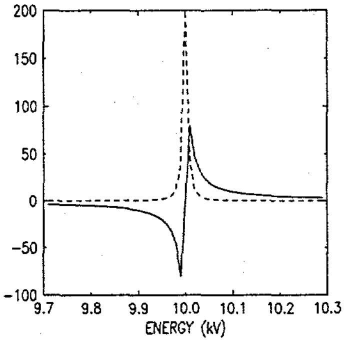

Figure 1. Calculation of the real (solid line) and imaginary (dashed line) parts in the bracket of Eq. (2)

3. EFFECTIVE DEPTH SENSITIVITY OF SURFACE SCATTERING

It is sufficient to consider the specular reflection from a single crystal surface for a discussion of the depth sensitivity of surface scattering. According to the uncertainty principle, we do not know which layer is the source of the measured intensity as long as the scattering is added coherently. Consider the scattered intensity from an ideally flat single crystal surface at the anti-Bragg condition. The scattered amplitudes from each layer are identical but the phases of consecutive layers are exactly opposite. The amplitude sum of the scattering from every pair of planes is therefore zero. The total scattering amplitude is also zero for an infinite crystal if we count the pairs starting with the top layer. However, the total scattering amplitude equals to that of *one* monolayer if we count the first layer by itself and count the pairs starting with the second layer. The absorption and extinction phenomena are ignored in this argument. However, including absorption and extinction effects will not solve the problem either. The magnitude of the total scattering amplitude is now uniquely defined: the scattering amplitudes are incrementally reduced from layers inside the crystal and the summation converges to a half. But, the origin of the scattering remains undefined. When the pairs are summed starting with the top layer, only a small fraction of the odd-layer scattering amplitudes are summed in phase to yield half a monolayer scattering amplitude, but this is not originating from the top layer. When the pair summation starts from the second layer, the small fraction of the odd-layer scatterings are again summed to half a monolayer scattering amplitude but with a phase opposite to that of the top layer; therefore, the overall sum of half a monolayer amplitude can now be considered to originate from the top layer.

Whichever the case may be, the scattering at any given Q must reflect the scattering factor of the top layer. For example, if we add a half monolayer on the surface, the total scattering at the anti-Bragg condition adds up to zero. This means that the scattering from the top half monolayer is the same in amplitude and opposite in phase with respect to scattering from the bulk. We can see from this example that the scattering at the anti-Bragg condition is fully sensitive to the top layer scattering density [8]. We now define the depth sensitivity in terms of x-ray momentum transfer. At the anti-Bragg condition (Q=G/2, where G satisfies Bragg condition), the wavelength of the momentum-transfer vector is two-layer long and only the top layer itself is in-phase. At this condition, we define the depth sensitivity 1 to indicate that only one layer is in-phase. At Q=G/4, the wavelength is four-layer long and top two layers are in phase (positive or negative together) and at Q=G/6, the top three layers are in phase, and so on. Therefore, the depth sensitivity is

$$S = \frac{1}{\sin^2(\pi Q/G)} \tag{3}$$

which is two times the calculated surface scattering intensity. That is, for a Q value small or close to G, the measured intensity is sensitive to S layers. This simple statement can be easily tested for different Q's. For example, S=1 for Q=G/2, S=2 for Q=G/4, S=3 for G=G/6, and so on. Therefore, this equation offers an *effective* depth sensitivity of the single-crystal reflectivity at various Q positions. Furthermore, it permits us to select Q positions that are sensitive to only the top layer, two layers, etc. In the case of off-specular scattering, of course, we must consider $Q_\perp$ instead of Q in Eq. (3).

4. COMPARISON OF CLEAN SURFACE DATA TO THEORETICAL CALCULATIONS

In order to take full advantage of the surface resonance scattering technique, the fine structures in the energy scans must be explained by a theoretical computation. However, unlike for the case of extended range fine structure (EXAFS), computational methods that include the near edge structure has not been available until recently. The computation for the near edge structure is complicated because solid-state effects must be properly included in order to reproduce the fine structure near the resonance energy of a ground state. Recently, such a computation scheme including solid state effects has become available[9]. In this section, this computational scheme will be used and the predictions will be compared to our data.

Since we have complete control over the depth sensitivity of the surface scatttaring, we can measure the near edge structure factor more accurately (without distortion due to absorption) than with any other techniques. When there is no change in the surface structure (no reconstruction or oxidation), one can measure the near edge structure factor by setting the x-ray polarization parallel to the surface. The measurements can be performed at a place in the reciprocal space where the measurement is sensitive to only a few surface layers in order to avoid the absorption effect. In Fig. 2, the computation (solid lines) is compared to the measured $|f_0 + f' + if''|^2$ shown as open circles in (a) [1] and to the measured f'' shown in (b) [10].

The computation is an ab initio calculation of f based on a simultaneous calculations of f' and f'' in the complex E plane. It is based on a real-space multiple scattering approach on a cluster of realistic atom models [9] in a self-consistent matter, thereby including the finite-size solid state effect. [This is unlike the approach by Cross et al.[11] where f' is calculated by combining the Kramer-Kronig transform of the popular x-ray xbsorption spectra(FEFF code) and the Cromer-Liberman computation[12].] Considering that only the scale parameter was adjusted to compare the data to the computation, the agreement is very good. The computation was carried out for 0 K since thermal effects will likely be negligible for the small electron momentum transfer at this energy range.

5. RESONANCE SCATTERING FACTOR FOR MODIFIED (OXIDIZED) SURFACES

The resonance scattering behavior of a *modified* surface is very different from that of the unmodified surface. A simple example is shown schematically in Fig. 3. In this example, the core-binding energy of the top surface layer is significantly shifted due to oxidation, and the normal negative singular resonance behavior of f' is modified by an additional positive singularity. The reason for this modification is that the singular behavior of the scattering from the top layer is opposite in phase and occurs at a different energy, than that of the bulk. As the figure demonstrates, the addition of two singularities at one resonance energy [shown in Fig. 3(a)] do not qualitatively change the shape of the singularity but that of two singularities at two different resonance energies can qualitatively change the resonance behavior as shown in Fig. 3(b). Platinum single crystal surfaces can be oxidized under electrochemical anodic potential con-

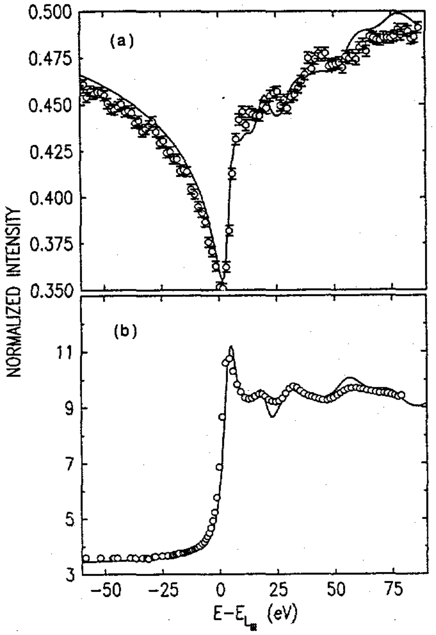

Figure 2. The computed and measured near-edge resonance scattering factor for clean, unmodified Pt(111) surface; (a) $|f_0 + f' + if''|^2$ and (b) f''.

trol. In our experiments with Pt(111) surfaces, at a certain oxidation potential the oxidation occurs via the so-called place-exchange mechanism where 0.3 monolayer of Pt–O dipoles are flipped over to minimize the dipole-dipole interaction energy. At this potential, the binding-energy of the platinum atoms in the place-exchanged 0.3 monolayer have shifted significantly, while the binding energy of the all other platinum atoms is unaffected [1]. At more positive potentials, further oxidation occurs and it leads to a layer of unstable oxide during the course of several hours. This is in the form of a mobile PtO_2 layer over the surface. Eventually the surface roughens, but there is a narrow time window when the core-binding energy of the top two layers (the top 0.3 monolayer place-exchanged and the second 0.7 layer un-exchanged layers) are significantly shifted by a deeper oxidation of the surface without significant roughening. Under these conditions, the most sensitive changes occur at Q=G/4, i.e. the condition where the two layers are in-phase. Since the two layers are in-phase, the energy scan at this Q value should be similar to that at the anti-Bragg condition for the oxide with only the top-layer atoms' binding energy shifted. An energy scan made for the two layer case at (0 0 0.8) is shown in Fig. 4 which is indeed very similar to the scan made at (0 0 1.5) for the oxide of the top layer only [1]. Since the surface platinum oxide is unstable, the x-ray intensity decreases gradually as the oxide layer becomes mobile and breaks down struturally. Indeed, this is the first direct evidence of oxidation-induced core-binding energy shift observed for an anodic oxide.

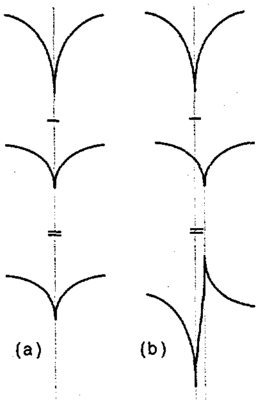

Figure 3. A schematic illustration of near resonance structure of $f''$for the case (a) where the resonance energies of the surface and bulk are identical and for the case (b) where they are different

6. CONCLUSION

In this paper we have shown that x-ray resonance scattering technique can be applied to surface scattering. By doing so, we demonstrated that surface specific chemical information can be obtained. We also demonstrated that a new computational scheme is available to explain the fine

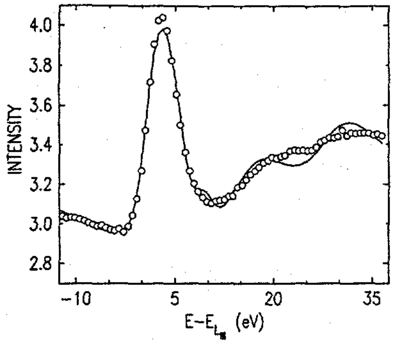

Figure 4. Energy scan of oxidized Pt(111) at (0 0 0.8). In this case, the binding energy of the top *two* layers has significantly shifted.

structure in the data, at least for a surface that can be prepared with an ideal termination without any chemical/structural modifications. We believe that further development of the computational scheme, including appropriate structure factors, can eventually lead to a complete understanding of the fine structure of our data. Then we will be able to study not only the chemical state of the surface oxide but also local and short-range structures. This technique is particularly useful in studying buried interfaces under electrochemical control; there is no other surface sensitive techniques that can be used to obtain similar information.

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