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Materials & Molecular Research Division

Presented at the International Conference on the Structure of Surfaces, Berkeley, CA, August 13-16, 1984

OPTICAL SECOND HARMONIC GENERATION FOR SURFACE STUDIES

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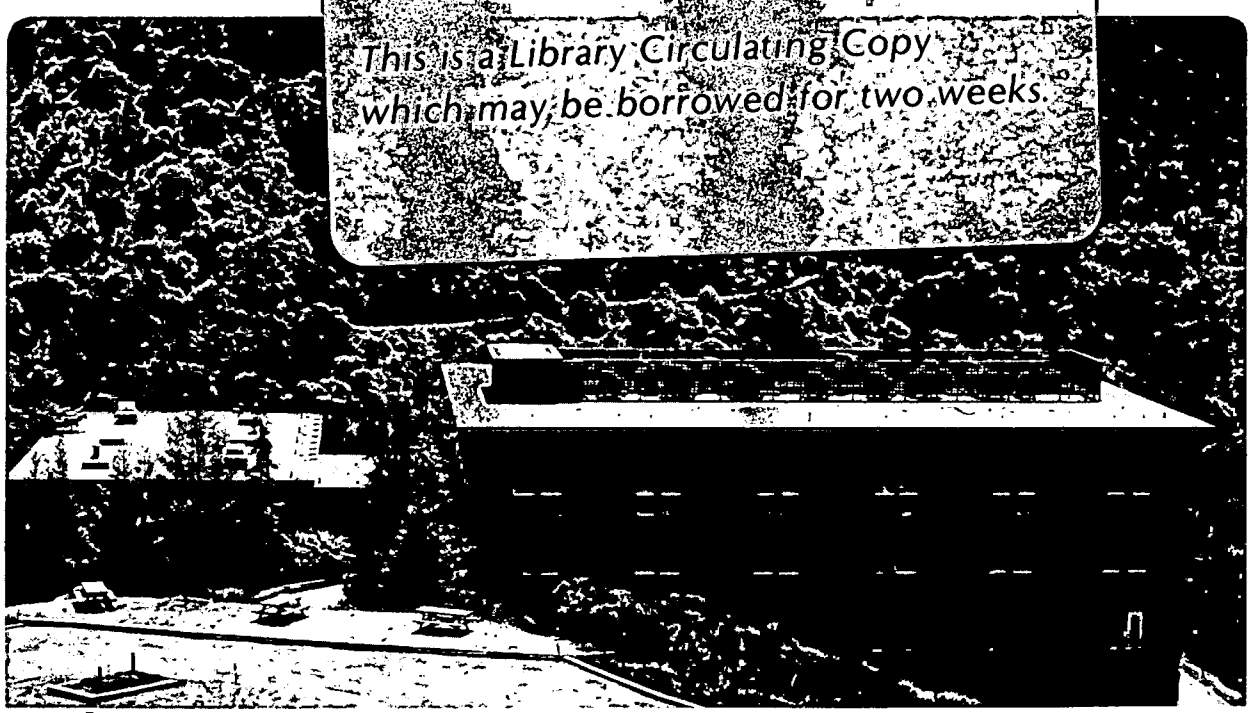

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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OPTICAL SECOND HARMONIC GENERATION FOR SURFACE STUDIES

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The progress of surface science lies heavily on our ability to probe surfaces and interfaces. For this purpose, many techniques have been developed in the past [1]. Recently, laser methods for material studies have advanced to a highly sophisticated level. One therefore wonders if they can also be applied to surface studies. Indeed, there have been a number of very interesting recent discoveries in this area. It is found that laser-induced fluorescence or resonant ionization can be used to probe angular, velocity, and internal energy distributions of molecules scattered or desorbed from a surface [2]. Coherent Raman spectroscopy [3], laser-induced desorption [4], photoacoustic spectroscopy [5], and photothermal deflection spectroscopy [6] can be used to study surface states and molecular vibrations of adsorbates. Lately, we have shown that surface second harmonic generation (SHG) is also an effective tool for surface studies [7]. We describe here some of our recent work on this topic.

Among the existing surface techniques, the optical ones are generally attractive for the following reasons: It has inherently a high spectral and time resolution; it is non-detrimental and suitable for remote probing; it can be applied to surfaces under high gas pressure or interfaces between two condensed media. The disadvantage is that the detection sensitivity is often low. Surface SHG obviously has all the vitures of the optical methods. As we shall see later, it also has enough sensitivity to detect a submonolayer of adsorbed atoms or molecules and enough flexibility to be useful for investigation of many different types of surface problems.

The basic idea of using SHG for surface studies is quite simple [7]. The SHG process is forbidden in a centrosymmetric medium, but allowed at a surface or interface. As a result, the SH signal generated from the interface between two centrosymmetric bulk media can dominate the SH signal from the bulk. In this sense, SHG is surface-specific. It is known that the typical value of a second-order nonlinear susceptibility is around 10^{-30} esu/molecule. From the solution of Maxwell equations [8], we can then show that the SH signal from a molecular monolayer with 10^{15} can yield 10^4 photons/pulse if a 1.06 μm laser pulse with a pulse energy of 40 mJ, a pulsewidth of 10 nsec, and a beam cross-section of 1 cm^2 is used. Since a detection system can easily detect an average signal of less than 1 photon/pulse, we readily see that surface SHG has the sensitivity of detecting a fraction of a molecular monolayer.

Experimentally, the submonolayer sensitivity of surface SHG has been confirmed at various interfaces: air/solid [7,9], liquid/solid [9], and air/liquid [10]. That the technique can be used for spectroscopic study of molecular adsorbates [7], for probing structural symmetry of a surface layer [7.11], for determining orientation of molecular adsorbates [9], and for measuring adsorption isotherm [9] has also been demonstrated. More recently, in order to show that surface SHG is also an effective method for studying well-characterized surfaces, we have carried out a ser-

ies of SHG measurements on both semiconductor and transition metal surfaces in an ultrahigh vacuum (UHV) chamber supported by LEED, Auger, and mass spectrometers [12,13]. We discuss briefly some of the results here.

The experimental arrangement for surface SHG, schematically shown in Fig. 1, is fairly simple. The SH output, which is coherent and highly directional, can be selectively detected through a filtering system. The samples used in our experiment were crystalline Si and Rh. Their oriented surfaces were cleaned in the UHV chamber by the usual procedure. Cleanliness of the surface and adsorbates on the surface were monitored by LEED, Auger, and thermal desorption spectroscopies. To avoid laser-induced damage or desorption of molecules, we kept the input laser fluence sufficiently low.

Transition metal surfaces are important for catalytical reactions [1]. We were interested in adsorption of O_2, CO, and alkali atoms on Rh(111) since they are related to catalysis for hydrocarbon formation and oxidation reaction. In all cases, we found that surface SHG was sensitive enough to detect the presence of submonolayers of adsorbates on the Rh(111) surface. A Nd:YAG laser at 1.06 μm or 0.532 μm with a ~ 7 nsec pulsewidth was used for the SHG measurements. The laser energy was kept at ~ 6 mJ and focused to ~ 10^{-2} cm^2. The SH signal from a clean Rh(111) surface was as large as 10^3 photons/pulse.

When the clean Rh surface was exposed to O_2, the SH signal decreased immediately in response to the adsorption of O_2 on Rh(111). This is shown in Fig. 2. The signal drops to 12% of the bare metal value at ~ 1.8 Langmuirs of O_2; the sharp 2 × 2 LEED pattern for a saturated oxygen layer was only observed when the exposure exceeded ~ 20 L. Oxygen appears on Rh(111) in the atomic form. Thus, the result of Fig. 2 is a clear demonstration of the capability of SHG to monitor time-resolved adsorption of submonolayers of atomic species. A model assuming that all adsorption sites are equivalent and noninteracting can be used to explain the result. Following the model, the surface nonlinear susceptibility can be written as

$$\chi^{(2)} = A + B\theta/\theta_s, \tag{1}$$

where A and B are constants, θ is the fractional surface coverage of oxygen with respect to Rh surface atoms, and θ_s is the saturation value of θ. In addition, the adsorption process should obey the Langmuir kinetics [1], which yields

$$\theta(t) = \theta_s[1 - \exp(- K\, pt/\theta_s)], \tag{2}$$

if the desorption rate is negligible, as is in the present case. Here, K is a constant accounting for the sticking coefficient, and p is the oxygen pressure. Knowing that the SH signal is proportional to $|\chi^{(2)}|^2$, and taking B/A and K/θ_s as adjustable parameters, we can actually use Eqs. (1) and (2) to fit the experimental result in Fig. 2 very well. That the Langmuir kinetics governs the oxygen adsorption on Rh has also been confirmed in the experiment by YATES et al. [14]. The value 0.93/L deduced for K/θ_s from our result agrees well with 0.78/L obtained by YATES et al., considering the limited accuracy of the pressure gauge.

The SH signal from Rh(111) also decreased rapidly upon adsorption of CO. We plot in Fig. 3 the measured SH signal as a function of CO surface coverage calibrated by LEED. The data exhibit a rather sudden change in slope at $\theta = 1/3$. This suggests that for $\theta \geq 1/3$, a new site may have appeared for CO adsorption on Rh. Indeed, previous studies [15] have shown that CO adsorbs to Rh on the top sites if $\theta \leq 1/3$, and on both the top sites and the bridge sites if $\theta \geq 1/3$. Using the model of noninteracting adsorption sites, we can again write the surface nonlinear sus-

ceptibility as

$$\chi^{(2)} = A + B\theta/\theta_s \qquad \text{for } \theta \leq 1/3$$

$$= A + B/3\theta_s + C(\theta - 1/3)/\theta_s \qquad \text{for } 1/3 \leq \theta \leq 3/4. \qquad (3)$$

With B/A and C/A taken as adjustable parameters, the expression of $|\chi^{(2)}|^2$ versus θ following Eq. (3) actually describes the experimental data very well, as shown in Fig. 3. The result here indicates that surface SHG is also site-specific for CO on Rh(111).

One may ask why the SH signal from Rh should decrease upon adsorption of either O_2 or CO. This can be understood as follows. For metals, the surface nonlinearity is generally dominated by delocalized electrons. It is known that oxygen and CO are electron acceptors. Their adsorption on metals would localize part of the delocalized electrons. Atomic or molecular adsorption on metals that results in electron localization would then reduce the effective surface nonlinearity if the adsorbed species is not as nonlinear as the metal surface. This being the case for O_2 and CO adsorption on Rh, we expect that adsorption of electron donors on Rh should increase the surface nonlinearity, and hence enhance the SHG. Alkali atoms are known to be effective electron donors. Figure 4 shows the SH signal as a function of surface coverage of Na, K, and Cs on Rh(111) at 210K with 1.06 μm laser excitation. Indeed, as expected, the signal increases monotonically with surface coverage for $\theta/\theta_s < 0.3$ in all three cases. For $0.3 < \theta/\theta_s < 2$, surface plasmon studies have suggested that interaction between adsorbed alkali atoms is important and the plasmon frequency increases from one associated with an electron-enhanced metal surface to that of a pure alkali metal surface [16]. This change of surface electronic properties is presumably responsible for the complex variation of the SH signal in this range. For $\theta/\theta_s > 2.0$, the SH signal is nearly a constant, indicating that it arises solely from the top two layers of alkali atoms. This, therefore, is another clear demonstration of the surface specificity ofSHG.

The presence of alkali atoms on Rh(111) should affect the adsorption of O_2 and CO. In Fig. 5(a), we show how SHG from Rh(111) with preadsorption of 0.6 monolayer of Na responds to exposure to CO. Compared with the case of adsorption of CO on bare Rh(111), the curve in Fig. 5(a) exhibits two, instead of one, sudden changes in slope, one at ~ 0.5 L and the other at ~ 2 L, suggesting that there are now three different adsorption sites for CO. Aside from the usual top and bridge sites, a new site, presumably close to Na, has appeared with a stronger binding energy. This conclusion is supported by the thermal desorption curve, monitored by SHG, in Fig. 5(b). The Na/Rh(111) surface was first saturated by CO coverage and then heated up at a rate of 15°C/sec. The desorption of CO began at ~ 200°C. In Fig. 5(b), the SH signal increases first slowly from 200 to 400°C and then rapidly from 400 to 450°C, indicating the desorption of CO from two sites with two different binding energies. After a narrow plateau, the signal rises again at ~ 520°C, showing the desorption of CO at the third site. It soon reaches the level of Rh with Na only, and starts to decrease at ~ 600°C. Finally, at ~ 800°C, the clean Rh(111) surface is obtained.

Previous studies [17] showed that CO adsorption on Pt(111) or Rh(111) can be greatly reduced by preadsorption of K. Using SHG to monitor, we have found the same for CO adsorption on Na/Rh(111). With a monolayer of Na on Rh, the signal dropped only 20% after 1200 L exposure. This is in sharp contrast to the result in Fig. 5(a), where the signal has dropped to 25% after only 2L exposure.

The SHG technique can also be used to study adsorbates on semiconductors, e.g., Si [13]. It is known that clean Si surfaces are generally

characterized by dangling bonds. Being highly asymmetric, these bonds are strongly nonlinear and contribute significantly to the surface nonlinearity of Si. Upon adsorption of atoms or molecules, such as oxygen, that quench the dangling bonds, the surface nonlinearity should decrease accordingly. We have used SHG to monitor the oxidation of Si surfaces. Figure 6 displays the variation of the SH signal from a Si(111) surface exposed to 10^{-6} torr of O_2 at room temperature and 800°C; the surface was initially cleaned and annealed, as denoted by the appearance of the sharp 7 × 7 LEED pattern. The room-temperature curve shows the decrease of SHG saturating at ~ 100 L. This agrees with the result of previous studies [18] that at room temperature, O_2 chemisorbs to Si(111) and forms an atomic monolayer at ~ 100 L exposure. At 800°C, the SH signal indicates that the oxygen monolayer is formed at ~ 30L. With longer O_2 exposure, the signal decreases much less significantly, and remains constant after ~ 80 L. It is known that at high temperatures, multi-layers of oxide can result on Si, but the SHG is apparently not very sensitive to the growth of more than one oxide layer because it no longer involves quenching of the dangling bonds. The oxygen atoms in these additional layers have lower binding energy than the chemisorbed oxygen, and can be more easily thermally desorbed than the latter. Indeed, the SH probe shows that the desorption rate of such oxygen is 5 times faster than the chemisorbed one.

SHG is also useful for investigation of bare Si surfaces. From simple symmetry argument, it is easily seen that the SH signal as a function of sample rotation about the surface normal should reflect the structural symmetry of the surface layer [7,11]. SHANK et al. [19] have actually used the technique to study laser melting. More recently, HEINZ and LOY [20] have succeeded in using SHG to monitor the transformation of the freshly cleaved 2 × 1 Si(100) surface to the annealed 7 × 7 surface.

What we have discussed are just a few examples of surface studies by SHG. They help in establishing SHG as a potentially useful surface tool. Numerous other possible applications of SHG to surfaces and interfaces are yet to be explored. In particular, surface dynamic studies with possible subpicosecond resolution, and studies of surface reactions under high gas pressure or in solution, are most interesting. A variation of the technique is the sum-frequency generation. With a tunable infrared laser, infrared spectroscopic measurements on surface states and adsorbates should become possible.

The UHV work described here was the result of a joint effort between Prof. Somorjai's group and our group. The following individuals deserve full credit: H. Tom, X.D. Zhu, C.M. Mate, and T.F. Heinz. J.E. Crowell also made a significant contribution. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

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FIGURE CAPTIONS

Fig. 1 Experimental arrangement for surface second harmonic generation.

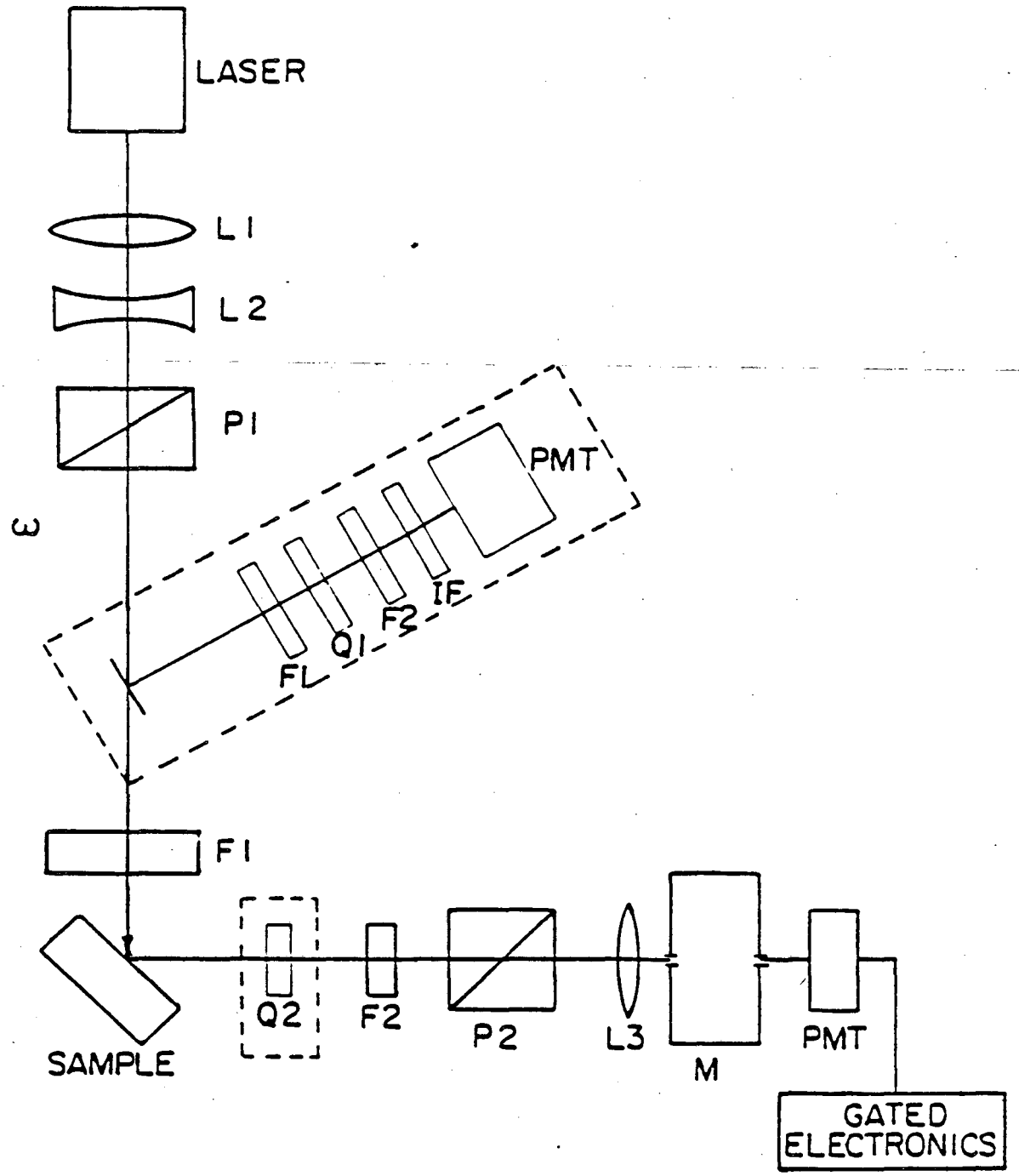
Fig. 2 Second harmonic signal from Rh(111) during O_2 exposure. —— experimental result; --- theoretical fit.

Fig. 3 Second harmonic signal from Rh(111) versus CO coverage. Solid curve is the theoretical fit.

Fig. 4 Second harmonic signal from Rh(111) versus alkali coverage.

Fig. 5 Second harmonic signal during (a) CO exposure from Rh(111) predeposited by 0.6 monolayer of Na, and (b) thermal desorption from Rh(111) predeposited by 0.6 monolayer of Na and saturated by CO adsorption.

Fig. 6 Second harmonic signal during oxidation of Si(111) at room temperature (RT) and at 800°C.



XBL 844-6831

Fig. 1

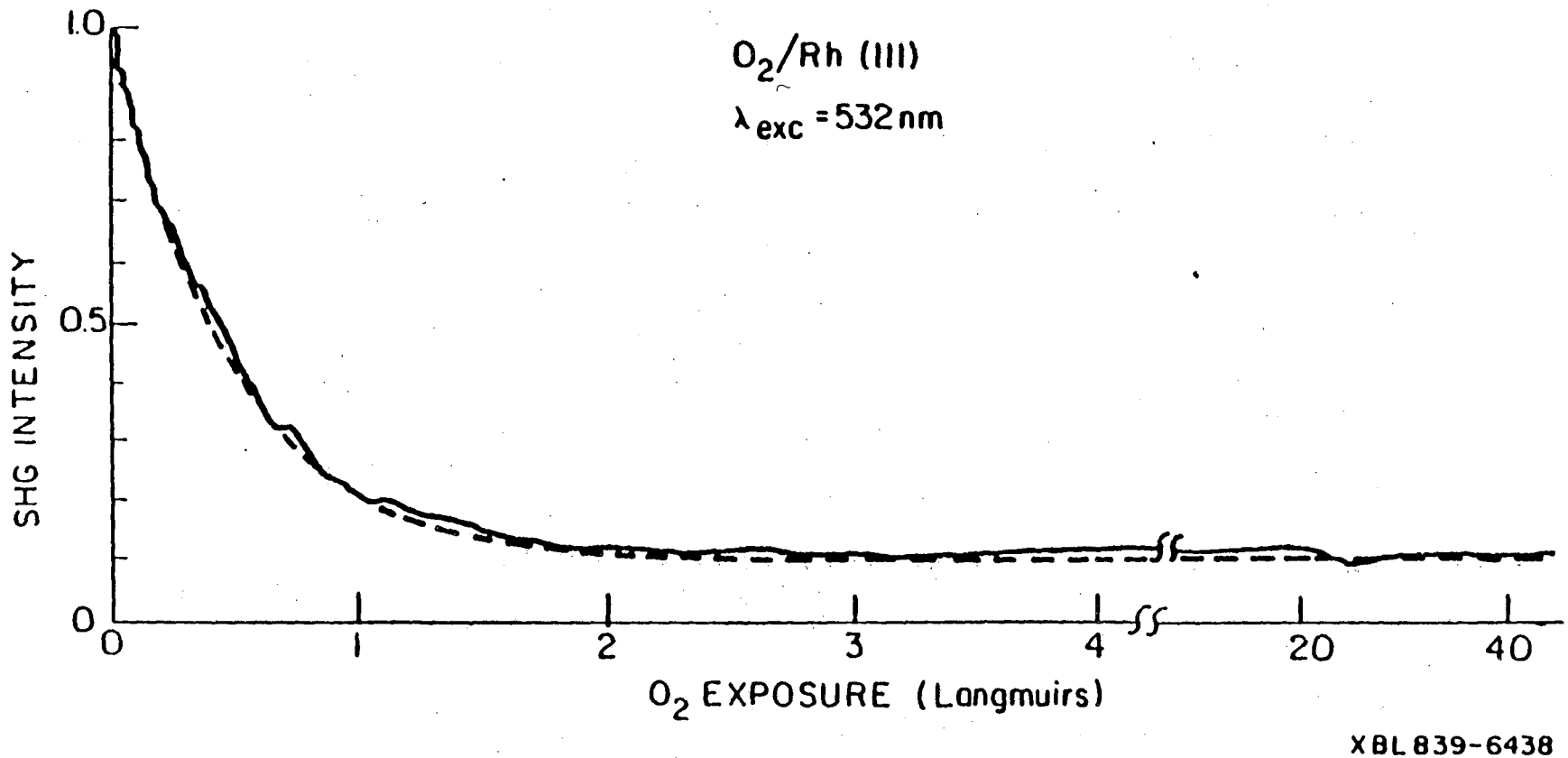

O_2/Rh (111)
λ_{exc} = 532 nm
SHG INTENSITY
1.0
0.5
0
0
1
2
3
4
20
40
O_2 EXPOSURE (Langmuirs)
XBL 839-6438

Fig. 2

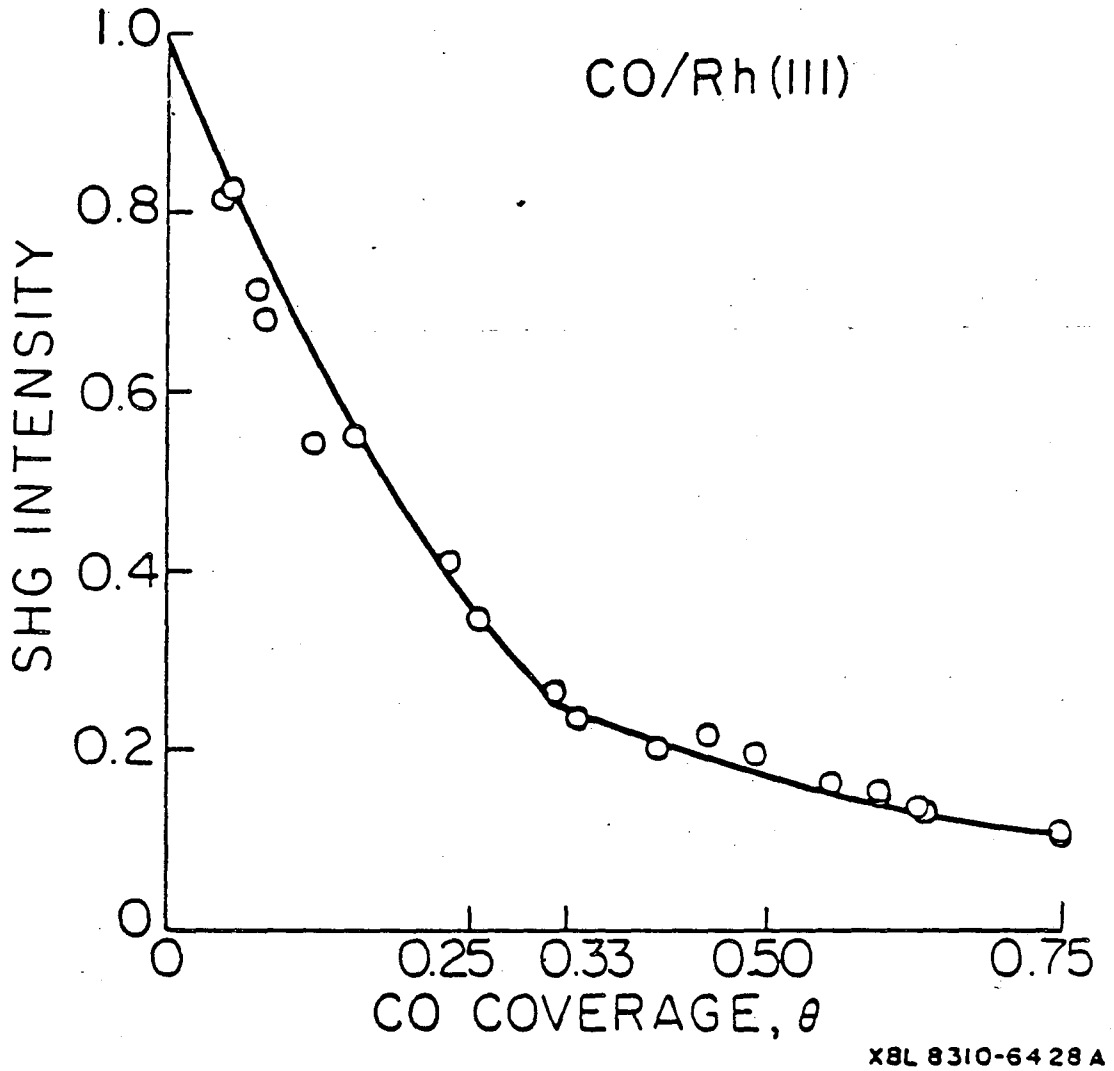

CO/Rh(111)
SHG INTENSITY
1.0
0.8
0.6
0.4
0.2
0
0
0.25
0.33
0.50
0.75
CO COVERAGE, θ
XBL 8310-6428A

Fig. 3

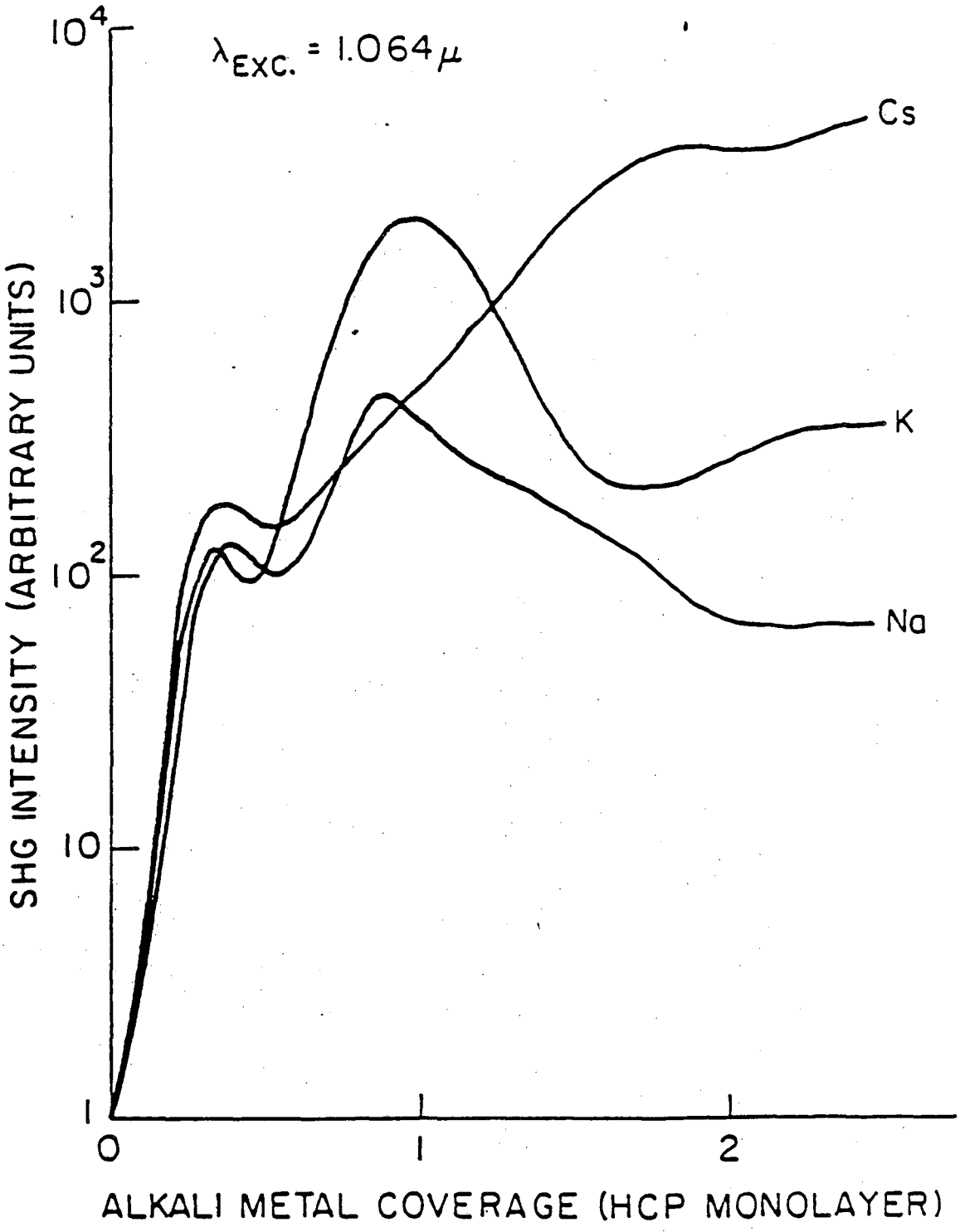


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Fig. 4

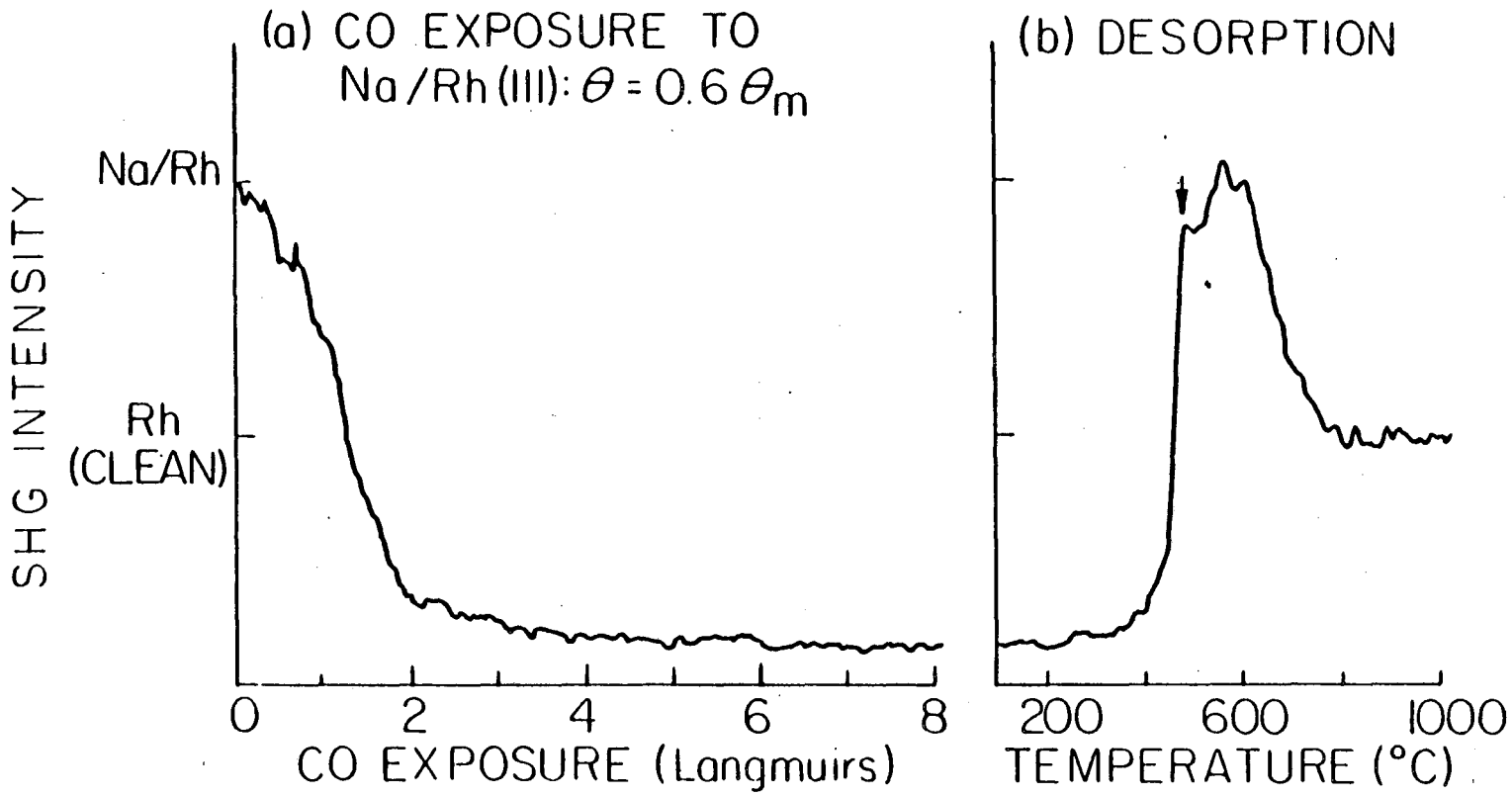

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Fig. 5

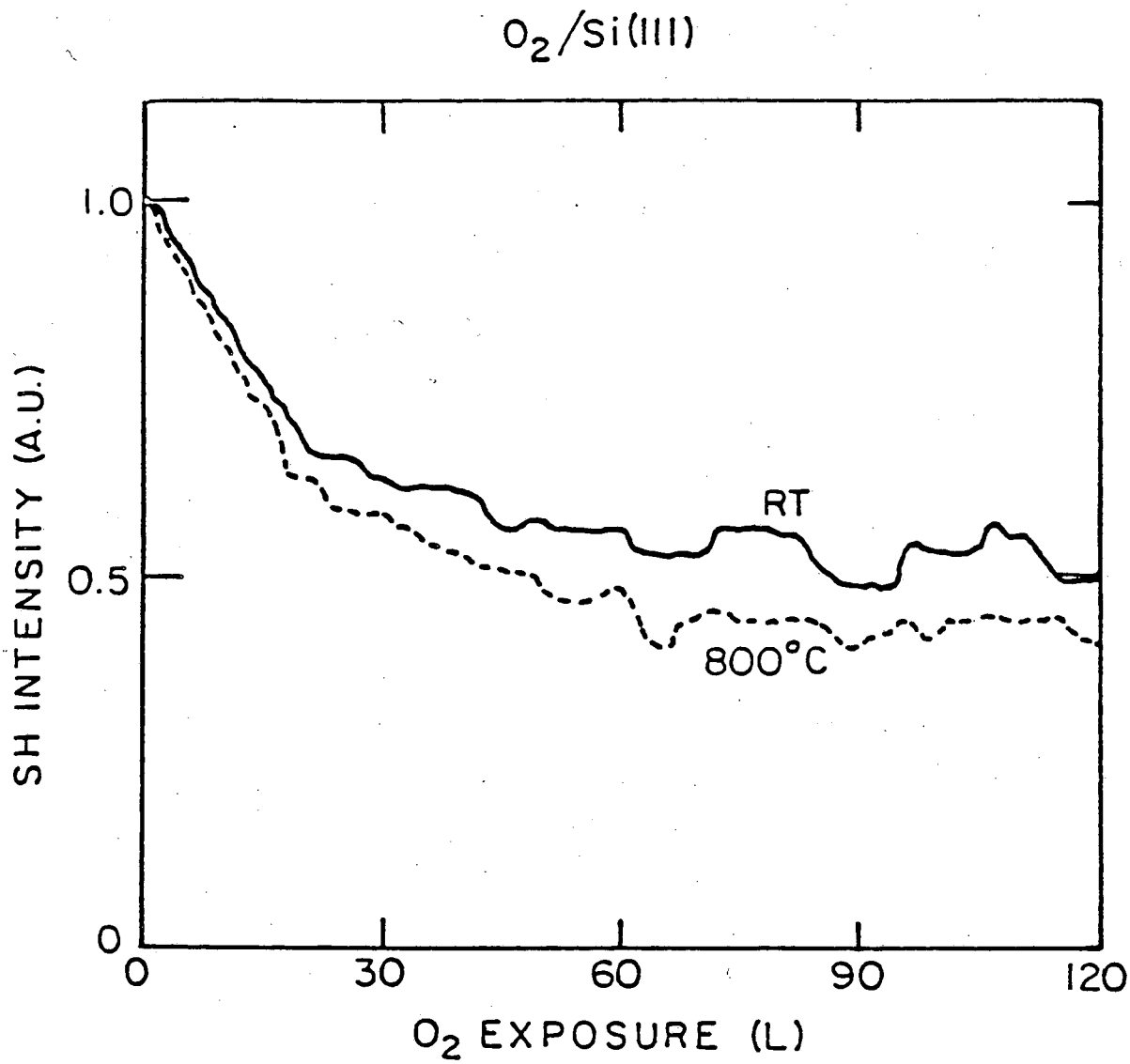

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Fig. 6

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