Can Pulsed Laser Excitation of Surfaces Be Described by a Thermal Model?

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In using pulsed laser excitation of surfaces to induce desorption or reaction of adsorbed molecules, it has generally been assumed that the absorbed energy is rapidly randomized, and a thermal model can be used to calculate the surface-temperature change. In this work, the transient temperature jump on a Ag(110) surface induced by an 8-nsec laser pulse is directly monitored with a psec probe pulse. The probe is based on a temperature-dependent second-harmonic-generation effect. The experiment provides the first direct evidence that the heat-diffusion model can correctly predict the magnitude and the time evolution of the temperature on the surface.

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The use of lasers to induce and probe chemical and physical processes on surfaces is a subject of much recent interest in surface science.[1] There are a few unique advantages in using lasers to excite an adsorbate/substrate system to induce surface reactions. The initial excitation is mode specific and may lead to the possibility of nonstatistical reaction channels. In many cases, however, thermalization of the initial excitation may be fast compared to the reaction rate, and all reactions would then proceed under thermal conditions. Even for this latter case of equilibration of the initially absorbed energy, the rapid ($>10^{10}$ deg/sec) temperature rise caused by pulsed laser excitation can change the relative yields of products coming from competing chemical pathways. The latter advantage has been demonstrated in studies of surface reactions.[2]

In order to correctly interpret the events following pulsed laser excitation of surfaces, it is essential to know the time scale of thermalization from the initially excited mode, and the resultant surface-temperature increase. An accurate account of the temperature evolution on the surface is essential to properly determine the kinetic parameters of the surface process.

Many surface studies have used powerful nanosecond laser pulses to excite metal substrates in order to induce surface processes.[2-9] In all cases, the transient temperature jump at the surface is not experimentally determined, but is calculated by a classical heat-diffusion model.[10,11] This model assumes that the energy absorbed into a specific mode thermalizes instantaneously and that the transfer of heat from the surface to the bulk can be treated by use of bulk heat-diffusion constants. Furthermore, several working assumptions have been widely used to reduce the complexity of the calculation, such as that higher-order terms in the heat-transfer equation can be neglected.

For excitation of metals using light from the near ir to the uv, intraband or interband electronic transitions are involved. Several femtosecond experiments have been performed recently for a variety of metals, where the rates of electron relaxation through electron-phonon collisions where shown to be of the order of several picoseconds.[12-15] Therefore, it is reasonable to assume that, on a nanosecond time scale, thermal equilibrium is established. The other assumptions in the thermal-diffusion model are more difficult to assess. The surface electronic and vibrational properties are known to be similar to, but not identical with, the bulk ones. Furthermore, it has been suggested[16] that higher-order terms in the heat conduction equation can be important as laser powers become greater than 1 MW/cm^2.

Despite these uncertainties, many studies rely on the results from this model to assess whether the induced process is thermal or nonthermal and to determine the kinetic parameters involved. However, whenever controversy arises, the validity of the model calculation is one of the first things to be questioned. So far, there has been only indirect experimental confirmation of the calculated transient temperature jump.[5,8] Because of the rapidity of the heating and cooling in pulsed laser excitation, which is typically several nanoseconds in duration, direct probing of the surface-temperature history has proven to be difficult.

Here, we introduce a technique based on resonant second-harmonic generation (SHG) that is capable of ultrafast measurement of surface temperature. SHG has recently been exploited in many studies because of its sensitivity to changes at an interface.[17-24] In the electric dipole approximation, SHG is forbidden in centrosymmetric media such as bulk metal crystals. This symmetry restriction is broken at interfaces, allowing SHG to occur. Thus, SHG is intrinsically sensitive to the electronic properties of the surface layer of atoms.

We have observed a strong resonance enhancement of SHG on a Ag(110) surface when 2ω is near the silver interband transitions at ~ 3.9 eV, as shown in Fig. 1. At different temperatures, the d and s electron-band structure changes, and causes a strong temperature dependence of the resonant SHG through changes in the nonlinear polarizabilities and dielectric constants.[25] This

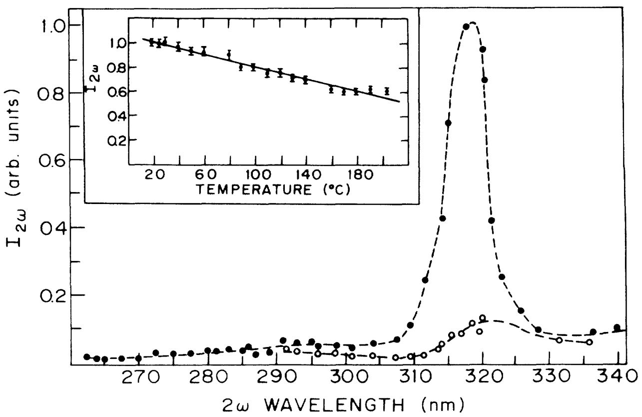

FIG. 1. Frequency dependence of *p*-polarized SHG on Ag(110) for *p*-polarized fundamental light with an incident angle of 60°. The filled points are at 94 K and the unfilled points are at 573 K. The dashed lines are drawn to guide the eye. Inset: The temperature dependence of *p*-polarized $I_{2\omega}$ for 628-nm, *p*-polarized fundamental light with an incident angle of 55°. The straight line is a least-squares fit of the experimental points, $I_{2\omega} = 1.059 - (2.494 \times 10^{-3})T$.

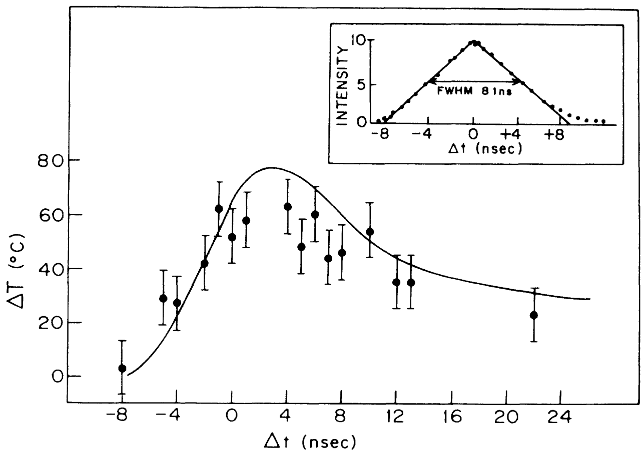

FIG. 2. Temperature change of a Ag(110) surface induced by a 1.064-μm, 8-nsec-FWHM, 125-MW/cm^2-peak-intensity laser pulse. The solid curve is calculated from the heat-diffusion model.

dependence can be used to determine the surface temperature. Since SHG occurs only within the laser pulse duration, fast-time resolution can be achieved if short laser pulses are used.

The use of SHG as an optical probe of temperature has several advantages over linear optical techniques. Linear reflectivity of metals can also change with temperature; however, the changes are usually much smaller than what we observe for SHG. For example, Paddock and Eesley have performed picosecond time-resolved reflectivity studies of a laser-heated nickel crystal and other metal films, where changes in reflectivity of about 10^{-4} were recorded.[26] Second, in contrast to the surface sensitivity of SHG, the linear reflectivity is sensitive to temperature changes throughout the entire optical penetration volume in the metal. Thus, it measures the integrated temperature change in the bulk. The surface temperature measured by SHG is localized within a few atomic layers of the surface, and is a more relevant quantity for surface processes since this is where adsorbates directly interact.

The second-harmonic intensity $I_{2\omega}$ from Ag(110), with ω set at 628 nm, decreases by a factor of 7 when the crystal temperature is changed from 94 to 675 K through resistive heating.[25] A section of this temperature dependence is shown in the inset of Fig. 1. The measured temperature dependence of $I_{2\omega}$ is used to determine the temperature jump induced by an excitation laser pulse. The pump-probe experiment is initiated by irradiation of the silver surface in an ultrahigh vacuum with a powerful 8-nsec pulse at 1.064 μm, followed at varying times by a much weaker picosecond 628-nm probe pulse, from which $I_{2\omega}$ is detected. A *Q*-switched Nd-doped yttrium-aluminum-garnet laser, whose 532-nm light is used to amplify the picosecond dye-laser pulse, also provides the ir pump pulses. The smooth, but slightly asymmetric, time profile of the ir pulse can be fitted by a triangular shape (FWHM=8 nsec) (see inset of Fig. 2).

The two beam waists at the Ag surface are carefully monitored: 1.8 mm diameter for the ir, and 1.4 mm for the dye beam. A measurement with a 100-μm pinhole mounted in front of a photodiode on an *x*-*y* translator shows a smooth profile for the ir-beam intensity. Within the probe-beam waist, the pump-beam intensity varies by less than 20%. Thus, the probe-beam samples an averaged temperature inside its waist. The averaged pump intensity on the Ag surface, corrected for the incident angle, is 125 MW/cm^2. Great care is taken to collimate the dye-laser beam so that its spot size does not vary as the delay is stepped over the length of more than 30 ft. At each delay, $I_{2\omega}$ was measured with the pump beam on and off, and its percentage change was converted to a change in temperature by using Fig. 1.

The measured change of surface temperature induced by the pump pulse is shown in Fig. 2. The peak of the pump intensity is defined as $t=0$. The temperature of the surface increases rapidly during the pump pulse, maintains a maximum from $\Delta t = 0$ to $\Delta t = 4$ nsec, and decays at a slower rate. The maximum 20% change in $I_{2\omega}$ corresponds to a 63 ± 10-K change on the surface.

The surface-temperature change can be calculated by the heat-diffusion model with the following simplifications: (1) The radiation absorbed by the metal is deposited at the surface ($z=0$). This simplification is justified for Ag, since the penetration depth of the 1.064-μm light, 125 Å, is small compared to the 10^5-Å diffusion distance of the heat during the pump pulse. (2) The heat flows in the dimension (z) perpendicular to the surface. Radial diffusion of the heat is neglected. (3) Radiative loss for the time scale of interest is small and is therefore neglected. (4) The temperature dependences of the heat capacity, thermal conductivity, and reflectivity are all assumed to be negligible, which is true for Ag for a temperature jump of 100 deg.[27] (5) Only first-order terms in the heat-transport equation are considered. Consequently, the temporal and spatial profile of the surface temperature, $T(r,t)$, can be determined from the classical heat-conduction equation,

$$\nabla\cdot \mathbf{J}(\mathbf{r},t)+\rho c\frac{\partial T(\mathbf{r},t)}{\partial t}=A(\mathbf{r},t)\,, \qquad (1)$$

where J is the heat flow, ρ is the density, and c is the specific heat. $A(\mathbf{r},t)$, the energy source term, is

$$A(\mathbf{r},t)=I_m(1-R)\alpha\exp(-\alpha z)f(x,y)q(t)\,, \qquad (2)$$

where I_m is the maximum laser intensity, R is the reflectivity, α is the absorption coefficient, and $f(x,y)$ and $q(t)$ are the normalized spatial and temporal profiles of the laser pulse.[11] In the simple case of a uniform $f(x,y)$, Eq. (1) has been solved to give the temperature at $z=0$ as

$$T(0,t)=I_m(1-R)(\pi Kc)^{-1/2}\int_0^{\tau} q(t-\tau)\tau^{-1/2}d\tau\,, \qquad (3)$$

where K is the thermal conductivity.[10]

The solid curve in Fig. 2 was calculated from Eq. (3) with $R=0.973$, $K=4.29$ W/cm deg, $c=6.06$ cal/mol deg, $\rho=10.5$ g/cm^3, and a triangular-shaped $q(t)$. The measured temperature profile is well described by the calculated curve. The maximum temperature and the characteristic rise and decay of the substrate temperature are correctly predicted by the above equations. Figure 2 represents the first direct experimental confirmation of the heat-diffusion model.

SHG is sensitive to temperature through the electronic response at the surface. As the temperature of the crystal is increased, the lattice expands, and the interband transitions change energy slightly.[28] Since SHG at 314 nm is resonantly enhanced by these interband transitions, the SHG efficiency changes. If the relaxation of the electronic excitation to the new thermally equilibrated lattice structure is not complete when the probe pulse arrives, the intensity of the second harmonic, of course, cannot be correctly related to a surface temperature via Fig. 1. The observation that the SHG response, as a function of time, mimics what one would expect for a surface whose temperature changes according to the heat-diffusion model is consistent with the assumption that the excitation energy is randomized faster than a nanosecond.

The correct predictions of the maximum temperature jump and the decay rate also justify the other assumptions used in the heat-diffusion model. However, further simplification of the model may not be warranted. For example, if the temporal profile of the excitation pulse is treated as a square wave form to reduce the complexity of Eq. (3), the temperature jump is overestimated by more than 40%.[29] On the other hand, it has already been shown that the calculation of the maximum temperature is not sensitive to the substitution of a triangular pulse for a Gaussian temporal profile.[29,30] The largest uncertainty in the application of the model calculation probably comes from the value used for reflectivity. It is important to measure the reflectivity of the particular sample being used, since reflectivities can vary greatly with the surface condition. In the case of silver, depending on the literature values for R can lead to errors as large as a factor of 5 in the calculated temperature jump; R for Ag films at 1.064 μm and $\theta=55°$ ranges from 97% (Ref. 31) to 99.5% (Ref. 32). This would introduce large errors in the determination of kinetic parameters in laser-induced surface processes, such as desorption or reaction.

Similar fast-time-resolved measurements of surface temperature can, in principle, be performed on other metals or materials where SHG is enhanced by electronic resonances. The variation of dielectric constants (or linear reflectivity) with temperature for gold, copper, platinum, palladium, and silicon suggests that SHG near interband transition regions may have a strong temperature dependence and can be used for such purposes. In addition, SHG can, in theory, be enhanced by specific surface electronic resonances. For example, SHG resonant with a surface state whose depth is temperature sensitive could be dramatically temperature dependent. Surface states have been observed for many clean metals, and often occur in the near-ir or visible wavelength regions.[33,34]

Even though our measurements have confirmed the complete thermalization of the absorbed energy on a nanosecond time scale and the usefulness of the heat-diffusion model on a Ag surface, the generalization of the predictive power of the model should be approached with caution. In cases where light is absorbed by the substrate, this model should be useful for calculating the surface-temperature change. However, if the excitation light is absorbed by the atomic or molecular adsorbates, the applicability of this model needs to be investigated. A calculation using only the substrate thermal diffusion constants depicts the surface-temperature change only if heat transfer into the substrate dominates the relaxation. The model may not calculate the true temperature of the adsorbates. For example, recently several studies have shown the unexpected efficiency of laser-induced desorption when a weak ir pulse is used to excite a vibration of a molecule adsorbed in multilayers on a surface.[5] The energy in the pulse is small enough so that the temperature rise of the surface as predicted by the heat-diffusion model is less than 1 deg. However, desorption of translationally or vibrationally hot molecules is observed, a process requiring a surface-temperature change orders of magnitude higher than the model prediction. Apparently, the energy absorbed by the molecules causes desorption before being dissipated by heat conduction into the bulk.

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