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Morphology dependent ultrafast electron dynamics in ultrathin gold films

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Ultrafast electron dynamics in 5 nm thick gold films have been investigated as a function of film morphology. The transient reflectivity data reveal a sub-100 fs rise time and a complex relaxation profile on the picosecond timescale. These data are discussed in terms of a modified two-temperature model of the electron dynamics accounting for the initial relaxation of the non-thermal population. The electron–phonon coupling may be sensitive to film morphology. The possible origin of this behaviour is discussed and results are placed in the context of enhanced photochemistry on thin metal films.

1. Introduction

The photochemistry and photodesorption of adsorbates at single crystal metal surfaces induced by visible and near UV radiation was exhaustively studied in the past two decades, and a number of excellent reviews have been published [1,2]. For most molecular adsorbates it was established (with a few exceptions [3]) that direct optical excitation is a minor channel and the dominant mechanism is substrate mediated hot electron attachment [4,1,2]. In this mechanism substrate electrons are excited by photon absorption to energies between the Fermi level and the photon energy. These 'hot' electrons may either relax through electron–electron and electron–phonon relaxation, or they may reach the surface, tunnel through the surface potential barrier and attach to an adsorbate affinity level. The adsorbate so excited may then undergo photochemistry with a yield and mechanism determined by the shape of the excited and ground state potential energy surfaces, and the lifetime of the adsorbate in the electronically excited state. The fate of the excited state is often well characterised by evolution on potential energy surfaces of the form proposed by Menzel, Gomer and Redhead [5,6] and Antoniewicz [7]. Copious evidence has accumulated to support this mechanism, including the dependence of the cross-section on the photon energy and polarisation [8], the translational and internal energy distribution [2] or the charge [9] of the desorbed product.

The key role of hot electrons in the primary processes of adsorbate photochemistry has focussed attention on the ultrafast dynamics of optically excited electrons in metals. Electron dynamics have been measured for a number of years, starting with the classical time resolved reflectivity measurements of Eesley and co-workers [10,11], a method which has been refined over the years [12,13]. More recently detailed insight into the dynamics of hot electrons and their interactions with adsorbates have also been obtained from two-photon photoemission measurements, which have been reviewed in detail [14–17]. These studies have shown that the hottest electrons, several electronvolts above the Fermi level, relax on the timescale of tens of femtoseconds.

A number of groups have investigated the possibility of modifications to the cross-section (and even mechanism) of adsorbate photochemistry through changes in the morphology of the metal surface. The topic has been reviewed in a recent work by Watanabe et al. [18]. Myli et al. and Goncher and Harris studied the resonant photodecomposition of large organic molecules on roughened silver in ultrahigh vacuum and reported enhancements due to resonance with the surface plasmon, assignable to field enhancements or enhanced chemistry at defects [19–21]. Kidd et al. studied the photodesorption and photodissociation of a number of small adsorbates on roughened silver [22,23], which had previously been shown to undergo hot electron induced photochemistry on a Ag(1 1 1) substrate [24]. On measuring the relative cross-section as a function of photon energy they found both a considerable enhancement in the cross-section, and also a resonance in the yield at around 350 nm. An example of such an enhancement is shown in Fig. 1a. This resonant behaviour is strongly suggestive of a role for surface plasmon excitation in the enhancement mechanism. Other groups have reported appreciably larger enhancements for photodesorption of NO from well characterised metal nanoparticles [25,18], rather than the roughened silver used in earlier studies. Again a resonant plasmon excitation mechanism was suggested. Very recently Hasselbrink and co-workers reported enhanced photochemistry on ultrathin single crystal metal films on semiconductor substrates, and observed a role for hot electrons excited in the semiconductor [26]. A general description of the

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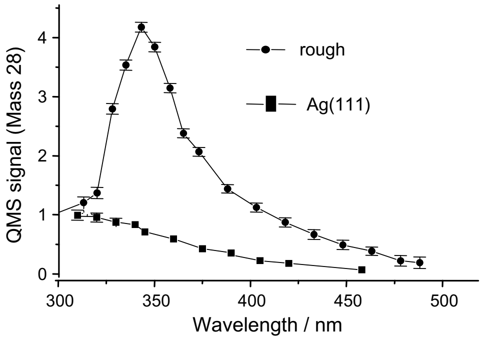

Fig. 1. The photochemical cross-section for the dissociation of OCS_a to CO_g and S_a as a function of the wavelength. Note the enhancement on roughened silver. Data from Kidd et al. [22].

possibility of enhanced photodesorption on thin continuous metal films was presented by Nest and Saalfrank [27].

There are several mechanisms which could contribute to plasmon enhanced photoprocesses in adsorbates. These are summarised in Fig. 2. Potentially the adsorbate mediated mechanism, which is known to be a minor channel on the single crystal surfaces, could be enhanced on the metal particle due to a very large enhancement in the electric-field at the surface. This mechanism, which is a major contribution to the surface enhanced Raman scattering mechanism, was discussed as a potential enhancement mechanism in adsorbate photochemistry some years ago [28,29]. However, we have compared the time of flight distribution of photoproducts from Ag(1 1 1) and roughened silver substrates, and find identical dynamics for both substrates [30]. Thus, the same substrate mediated mechanism appears to operate on both roughened and single crystal surfaces.

An alternative electric-field enhancement mechanism was discussed by Monreal and Apell [31] and invoked in connection with non-thermal evaporation from photoexcited metal clusters [32]. In this mechanism the enhanced electric-field at the surface favours surface electron hole pair excitation which creates hot electrons directly at the surface, and may thus enhance the probability of electron attachment to the adsorbate. Another route to an enhanced population of hot electrons is through the excitation of the particle plasmon resonance. The plasmon excitation corresponds to a collective excitation of electrons in the particle. However, it is established that the plasmon is very short lived and that a major decay pathway, called Landau damping, is into single particle (hot electron) excitations. This enhanced population of hot electrons may contribute to the observed resonant enhancement. Finally it is possible that the lifetime of the hot electrons themselves are a function of the substrate morphology, and a longer lifetime on a roughened or nanoparticulate surface may contribute to an enhanced photochemical cross-section.

The last three enhancement mechanisms mentioned above all in some ways require an understanding of the morphology dependence of the hot electron dynamics. This in turn suggests that a simultaneous investigation of electron dynamics and surface morphology will be informative. As a step in this direction we report here the ultrafast transient reflectivity of 5 nm thick gold films deposited on BK7 prepared with different substrate treatments, leading to variable morphologies. The morphology is measured by atomic force microscopy (AFM) and transmission spectroscopy (see Fig. 3).

The remainder of this paper is structured as follows. The next section is concerned with experimental methods and gold film preparation, which is followed by a description of the transient reflectivity as a function of morphology of the ultrathin films. These data are then discussed in terms of the relationship between reflectivity change, electron dynamics and morphology. This paper finishes with some conclusions and speculations on the significance of the observations for enhanced adsorbate photochemistry.

2. Experimental

Ultrafast transient reflectivity is recorded using a basic pump and probe apparatus. The lasers source was a home-built cavity dumped titanium sapphire laser, described in detail elsewhere [33]. Pulses at a repetition rate of 300 kHz, temporal width 30 fs and energy of a few tens of nanojoules at a centre wavelength of 830 nm were divided in a 4:1 ratio at a beamsplitter. The more intense pump beam was modulated by a mechanical chopper and focussed onto the gold surface. The probe beam was spatially overlapped with the pump on the surface but with an orthogonal polarisation to prevent coherent effects from the scatter generated on the surface. The intensity of the reflected probe was measured by a photodiode via a polariser. The output of the diode was routed to a lock-in amplifier which measured the modulated reflectivity, ΔR. At the same time the total reflected intensity, R, was measured from the integrated diode output and these were combined to yield the ratio $\Delta R/R$ directly.

BK7 substrates with a flatness of $\lambda/4$ were initially cleaned thoroughly [34–37] prior to vacuum deposition of pure gold (Aldrich, 99.99%) at a rate of 0.02 nm/s, as monitored by a quartz crystal microbalance. All films were prepared with a thickness of 5 nm.

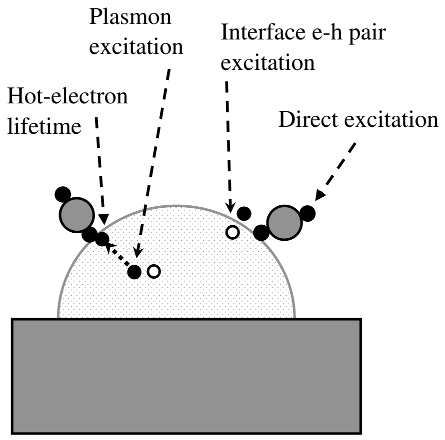

Fig. 2. Some plausible mechanisms for surface morphology enhanced adsorbate photochemistry.

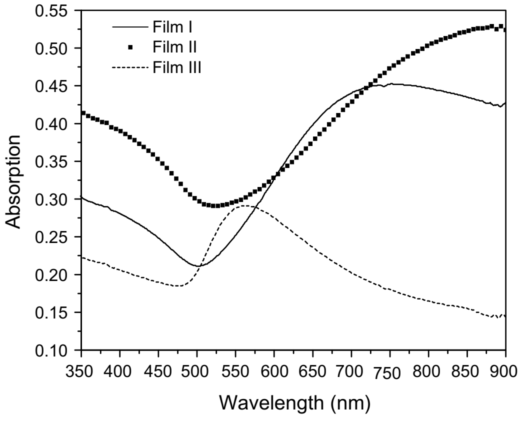

Fig. 3. Transmission spectra of the films I (solid), II (dashed line) and III (dotted line).