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Real-Time Investigation of Potassium Growth by Surface Differential Reflectance Spectroscopy

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The growth of potassium discontinuous films onto a low-temperature oxidized silicon substrate has been followed in real-time by surface differential reflectance spectroscopy. The energy positions of the plasma resonances in the potassium particles and their changes as a function of the amount of potassium are related to the shape of the particles and to their interaction. Three stages in the formation of the film are determined: (i) nucleation of small spherical particles, (ii) growth and flattening of the particles, (iii) coalescence.

The determination of the morphology of supported metal films is an important goal for technological applications. However, it is usually achieved by microscopic techniques which can be used only after the end of growth [1 to 3]. The real-time surface differential reflectivity spectroscopy (SDRS) is a technique which gives the possibility to follow the changes of reflectivity of a given surface, for example, due to the formation of an overlayer. In order to illustrate the ability of SDRS for monitoring the growth of a metal film, we have studied the formation of a potassium film grown at low temperature on an oxidized silicon substrate. The choice of an alkali metal, whose optical response is well-described by use of a free-electron metal model, should give the possibility to relate the SDR spectra to the morphology of the film, namely to the shape of the K particles formed on the substrate and to the interaction between them. Actually, we identify three stages in the formation of the K film: 1. nucleation of non-interacting spherical particles (low density case); 2. growth and flattening of the particles, together with electromagnetic interaction between them (large density); 3. coalescence of the particles.

The silicon substrates were chemically prepared by an HF treatment followed by an oxidation using a mixture of hydrogen chloride and hydrogen peroxide [4]. This resulted in a silicon dioxide, whose thickness was ≈ 2.2 nm, as measured by ellipsometry. Potassium was evaporated in the vacuum chamber whose base pressure was 1×10^{-8} Pa, from a SAES getter which had been previously outgassed in order to avoid oxidation of potassium. The substrate was maintained at -120 °C in order to prevent re-evaporation of K which occurs at room temperature [5]. The flux of K atoms arriving at the surface was estimated to be $\approx 10^{-2}$ atom/nm²/s [6], which corresponds, for bulk K density, to a mass thickness of 6.7×10^{-4} nm/s. The optical measurements were performed during the K deposition by use of an in-situ differential reflectivity spectrometer, the complete description of which is given in [7]. The measured quantity is the

relative change of reflectivity of the substrate upon deposition of K,

$$\frac{\Delta R_p}{R_p} = \frac{R_p[\text{K/Si}] - R_p[\text{Si}]}{R_p[\text{Si}]}, \quad (1)$$

where $R_p[\text{K/Si}]$ and $R_p[\text{Si}]$ are the reflectivities of the oxidized silicon substrate with and without potassium, respectively. The spectra were recorded every 10 s, which permitted us to follow in real-time the growth of the K film. In order to increase the signal-to-noise ratio, the experiments were performed in p-polarization, at an angle of 60° , smaller than the Brewster angle of silicon which is about 75° . This led to an increase of the signal by a factor of 25 in comparison to the one which would have been measured in normal incidence. Moreover, it can be shown that optical absorption in the K layer for the electric field perpendicular (respectively parallel) to the silicon surface yields a negative (respectively positive) maximum in the DR spectra, which gives the possibility to distinguish between parallel and perpendicular resonances.

In the very first stages of potassium deposition, a certain amount of K atoms migrate through the oxide down to the SiO_2/Si interface, where they remain as K^+ ions, as shown by Auger spectroscopy and DR measurements [8]. After this initial stage, the migration of K atoms stops and particle formation starts on the surface of the oxide. Fig. 1 presents the experimental DR spectra as function of the energy of light for increasing amounts of K, indicated by the mass thickness t_m of K in nm. Three different stages in the growth can be observed. For the smallest values of t_m (0.05 and 0.08 nm), a single minimum in DR is observed around 1.9 eV; then this minimum progressively shifts to a value of 2.7 eV when the amount of K increases, and simultaneously broadens. For larger evaporation times, this minimum stays at the same position, while a second minimum appears at 3.4 eV which becomes dominant. As indicated previously, the minima (i.e. negative maxima) in the DR spectra are due to optical resonances in the K film, perpendicular to the substrate. It is known that, for free-electron metal spheres, a Mie dipolar resonance (surface plasmon-like) can be excited by light at an

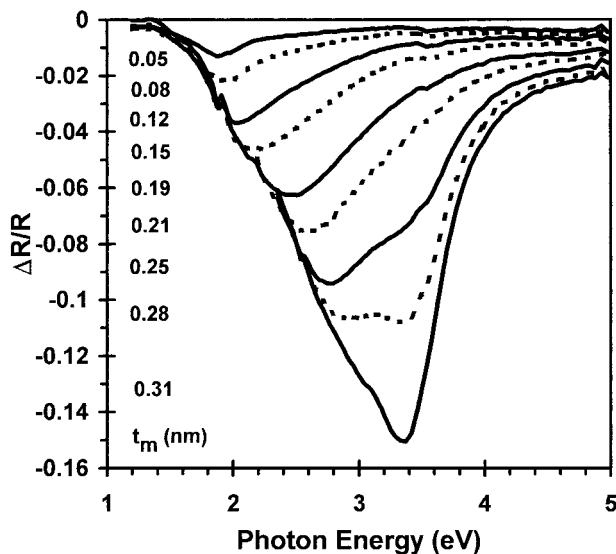


Fig. 1. Experimental DR spectra in p-polarization for increasing amounts of K grown on an oxidized silicon substrate. The mass thicknesses t_m are indicated in the figure

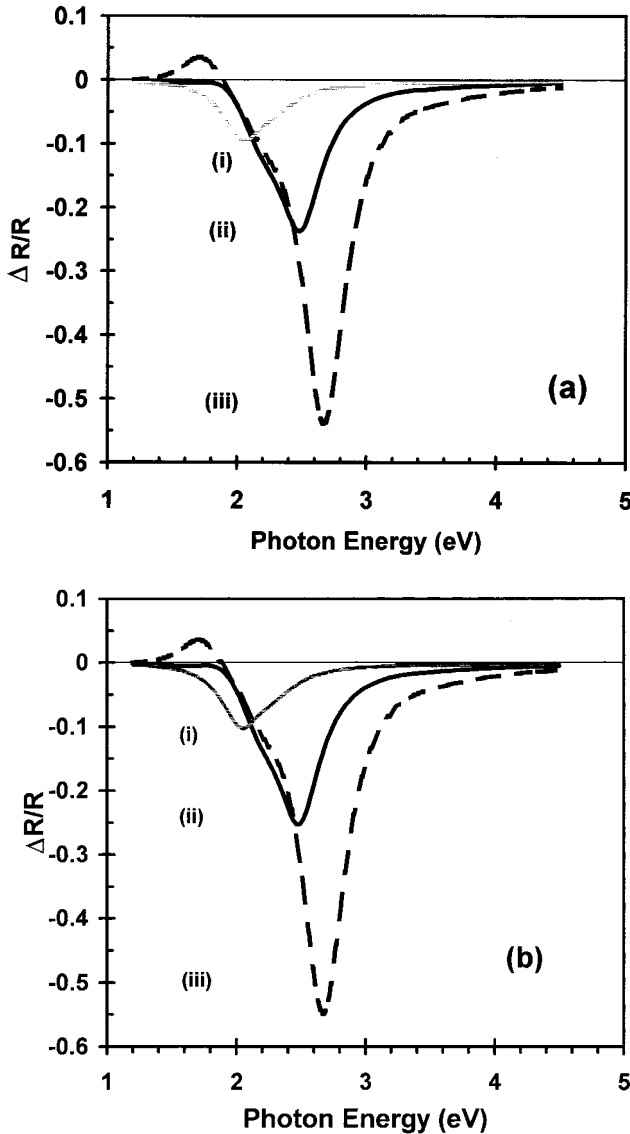


Fig. 2. a) Calculated DR spectra for interacting K spheres with increasing filling fractions; (i) small f_2 (no interaction), (ii) $f_2 = 0.25$ and (iii) 0.5. b) Calculated DR spectra for oblate spheroidal particles with different aspect ratios (i) $r_0 = 1$, (ii) 1.5, and (iii) 2. In both cases, the mass thicknesses have been taken equal to (i) $t_m = 0.04$, (ii) 0.1, and (iii) 0.21 nm

energy $\hbar\omega_D = \hbar\omega_p/\sqrt{3}$, where ω_p is the plasma frequency of the metal. For potassium, the plasma energy is $\hbar\omega_p = 3.8$ eV [9], leading to a dipolar resonance for isolated K spheres at the energy $\hbar\omega_D = 2.2$ eV. However, the electromagnetic interaction of the particles with the substrate leads to a red-shift [10]. This interaction is usually taken into account in the dipolar approximation, where the substrate is replaced by an image-dipole [1]. It has been shown recently that, for an exact treatment of the interaction with the substrate, not only the dipole coupling, but also the multipole coupling (MC) has to be considered, which increases the red-shift of the

dipolar resonance and yields additional features due to multipolar resonances. In our case, the slight shoulder around 2.3 eV in the 0.05 and 0.08 nm spectra – although not clearly visible with the scale chosen here – is an effect of this MC with the substrate, which has been discussed in a previous paper [11]. We shall now consider the two first stages, namely the single resonance initially located at 1.9 eV, then shifting to 2.7 eV. Fig. 2 shows the calculated DR spectra of K spheres with increasing densities onto the Si substrate. The mass thicknesses have been chosen, for comparison with the experiments, equal to 0.04, 0.10 and 0.21 nm. The electromagnetic interaction between the spherical K particles and the substrate including the MC has been treated by use of a multipolar model developed by Wind et al. [12]. However, an exact treatment of the

interaction with the silicon substrate covered by the silicon dioxide is a difficult task. We have considered here only the interaction with the silicon dioxide. As we have previously shown, this gives a satisfactory result, although the multipolar effects are in this case slightly reduced [11]. In all the calculations presented here, we have used a Drude expression for the dielectric function of potassium, with a plasma energy equal to 3.8 eV [9] and a damping parameter $\hbar\tau^{-1} = 0.4$ eV, whose value is supported by photo-absorption experiments on small isolated K clusters [13]. Curve (i) of Fig. 2a is the calculated DR spectrum for K spheres onto the Si substrate in the low density limit, where the particles are far away not to interact with each other. The agreement with the low amount experimental spectra is rather fair, although the position of the resonance is a little too high, which can be explained, as indicated above, by the fact that the electromagnetic interaction with the substrate is underestimated in our calculations. The blue-shift and the broadening of the resonance for larger evaporation times observed in the spectra of Fig. 1 can be explained by two effects: the electromagnetic interaction between the particles and a progressive flattening of the particles when they grow. In order to illustrate the first effect, Fig. 2 displays also the DR spectra for a collection of K spheres on the substrate with increasing filling factor $f_2 = 0.25$ and 0.5 . Here, the two-dimensional filling fraction f_2 is defined as $f_2 = N\pi b^2/A$, where b is the radius of the spheres and N the number of spheres on an area A . The maximum value of f_2 , obtained for an hexagonal close-packed distribution of the spheres, is $\sqrt{3}/\pi = 0.55$. The relation between f_2 and t_m is

$$t_m = \frac{4}{3} b f_2. \quad (2)$$

The interaction between the particles has been taking into account following the approach of Wind et al. [12]: first, the effective polarizability of the spheres interacting with the substrate is calculated in the multipolar model, then the dipolar interaction between the spheres is considered alone. The calculated resonance shifts to 2.6 eV for $f_2 = 0.5$, which is close to the position of the resonance observed for $t_m = 0.21$ nm. This effect can be explained easily if each effective dipole is regarded as an harmonic oscillator. The electric field perpendicular to the substrate, created by the neighboring dipoles and acting on a given dipole, increases the restoring force of the dipole, yielding a shift of the resonance frequency to larger values [10]. However, after (2), the radius of the spheres would be equal to 0.3 nm for $f_2 = 0.5$, which is clearly not realistic. This shows that a simple interaction between the K particles, which have initially a spherical shape, cannot explain the important observed shift. We will now study the effect of flattening of the particles. The simplest model for a flat particle is an oblate spheroid, with an aspect ratio r_o defined by $r_o = b/a$, where a and b are the small and large axes respectively. The perpendicular resonance (i.e. parallel to the rotation axis a) for an isolated spheroid, shifts from $\hbar\omega_p/\sqrt{3}$ for the sphere to $\hbar\omega_p$ for an infinitely flat spheroid. Fig. 2b shows the results of the calculation for the supported spheroids with increasing aspect ratios r_o from 1 (sphere) to 2, taking into account the multipolar interaction with the silicon dioxide. No interaction between the particles has been considered here, in order to isolate the effect of the shape. The same values for the mean thicknesses as in Fig. 2a have been taken. It can be seen that the spectra are almost identical to the ones drawn in Fig. 2a. The effect of interaction between neighboring spheres on a substrate is the same as the effect of the flattening of the particles. This means that optical measurements, if they are taken alone, cannot distinguish between both effects. In our case, because of the relative small filling fraction, it is

clear that the observed shift comes mainly from the flattening of the particles, while the interaction between the particles has a smaller effect, at least at the beginning of the growth. This broadening is consistent with microscope observations performed, for example, on Sn and Ga droplets [3]. The larger intensity of the theoretical curves with respect to the experimental ones can be explained by the important broadening of the resonance observed in the experiment. This is likely due to the distribution of the shapes of the particles around an average shape which leads to a peaking of the resonance at 2.7 eV for $t_m = 0.21$ nm, but also to some uncertainty in the determination of the flux of atoms and of the sticking coefficient.

For larger amounts of K ($t_m > 0.25$ nm), it is seen in Fig. 1 that the resonance at 2.7 eV does not shift anymore. On the other hand, a second resonance appears at 3.4 eV and increases in intensity. For much larger amounts of K (not shown here) the 2.7 eV negative maximum is not visible anymore, and the only feature is the 3.4 eV one. Contrarily to the previous case, this new resonance cannot be due to the continuation of the progressive flattening of the particles, but to the abrupt appearance of new particles with a much flatter shape. We interpret this as the signature of the beginning coalescence between close particles. In order to illustrate this, we have drawn in Fig. 3 the DR spectra calculated for oblate spheroids with a larger aspect ratio $r_o = 6$. In this case, in order to take into account the actual morphology of a film at the coalescence, a filling fraction f_2 equal to 0.3 has been chosen. Different values of f_2 (from 0 to 0.5) shift the resonance to slightly smaller or larger energy. The position of the resonance in the calculated curve is the same as the position observed in the experimental spectra. When coalescence occurs, the particles which are grouped together suddenly change their shape and become flatter, which is reproduced by a larger energy resonance. In the first stage of the coalescence, both kinds of particles are present on the surface, yielding to the two negative minima displayed by the 0.25 to 0.31 nm experimental spectra.

Finally, the growth of the K film can be followed by drawing the intensity of DR for two typical energies, say 1.9 eV which corresponds to the initial resonance for the spher-

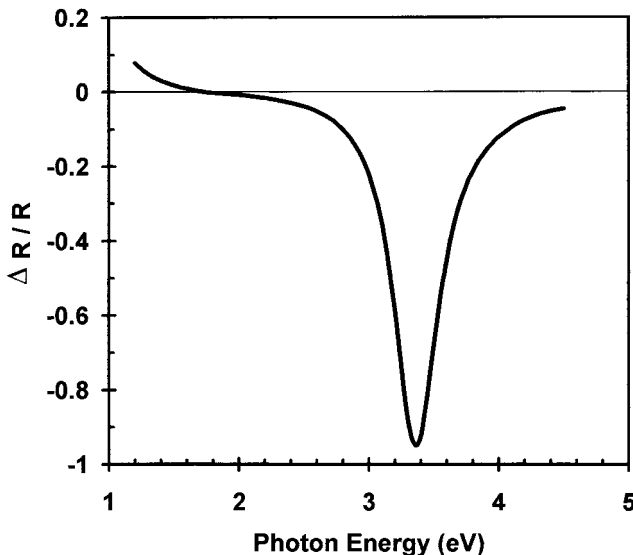


Fig. 3. Calculated DR spectrum for oblate spheroids with $r_o = 6$ and a filling fraction $f_2 = 0.3$. The mass thickness is $t_m = 0.3$ nm

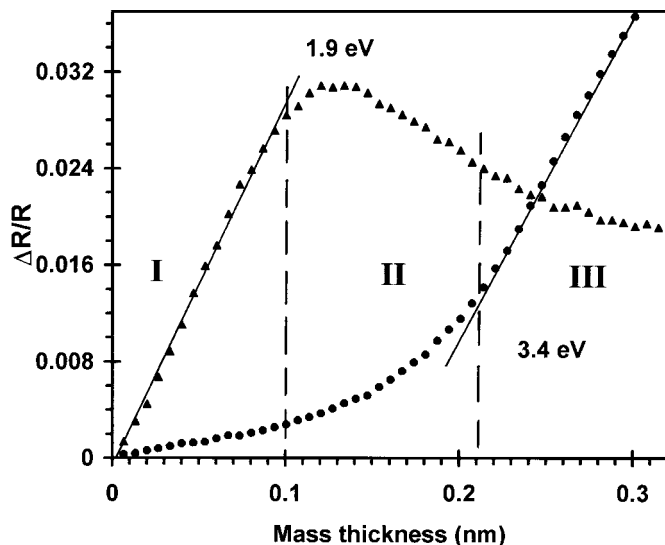


Fig. 4. Change of the experimental intensity of the DR signal at two photon energies, 1.9 and 3.4 eV, as a function of the mass thickness t_m

ical K particles, and 3.4 eV which is the resonance of the coalescing particles. This is drawn in Fig. 4 as a function of the mass thickness. We can clearly identify the first stage, where the 1.9 eV signal increases linearly, what we interpret as the nucleation stage of the particles with a spherical shape (region I in Fig. 4). The second stage (II) corresponds to the growth of the particles where the particles become flatter: the resonance shifts to larger energies, therefore, the 1.9 eV signal increases with a slower rate and eventually decreases. The third stage (III) is observed by the faster increase of the 3.4 eV signal. This corresponds, as explained above, to the coalescence of the particles, which takes place here from a mass thickness of about 0.21 nm.

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