

## Continuous Monitoring of Mg Oxidation by Internal Exoemission

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Thin-film Mg/Si(111) Schottky diodes are exposed to oxygen to detect chemicurrents in the devices. The detected charge is created by nonadiabatic energy dissipation and due to either internal exoemission currents or surface chemiluminescence induced photocurrents. Both contributions can be distinguished by changing the metal film thickness of the device. Auger electron spectroscopy to study the oxygen uptake demonstrates that the chemicurrent transients represent truly the time dependent reaction rate at the surface. Model calculations indicate that the current monitors Mg oxide island nucleation and growth.

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The interaction of oxygen molecules with uncovered reactive metal surfaces deposits energies of typically a few electron volts per reaction on the surface [1,2]. The chemical energy that is dissipated nonadiabatically becomes evident by exoelectron emission (EEE) into vacuum and surface chemiluminescence (SCL) [3–9]. The oxidation of clean Mg surfaces is an example for EEE and SCL [4,7–9]. Upon oxygen exposure, the chemisorptive emission of electrons from Mg is delayed. After an induction period where no emission is observed the EEE current increases with exposure time, reaches a maximum and, eventually, levels off toward zero. The length of the induction period depends on the molecule flux. This period and the slow increase of the EEE currents have been related to the reduction of work function with increasing oxygen coverage allowing more electrons to traverse the surface potential barrier. However, this explanation is rather speculative since the reaction kinetics or the electron excitation cross section may be coverage dependent as well what may produce similar EEE curves.

To elucidate the EEE current transients, the emission phenomena must be distinguished from the change of work function. This may be achieved by chemicurrent measurements. Here, thin-film electronic devices are used to detect electron-hole pairs within the device which are generated by exothermic surface reactions [10–12]. The present study applies the chemicurrent method for the first time to an EEE/SCL system, i.e., the oxidation of Mg surfaces. It demonstrates that the chemicurrent represents the chemical kinetics of the oxidation and is not influenced by changing properties of the device. It is therefore a method to investigate the kinetics without interrupting the exposure typical for spectroscopic studies.

The energy-space diagram in Fig. 1(a) depicts schematically the principle of chemicurrent detection with thin-metal film Mg/*p*-Si(111) Schottky diodes. For Mg/Si, *p*-type diodes have larger barrier heights than *n*-type devices and provide a lower noise level. The thickness *d* of the Mg layer is in the range of mean free paths of excited charge carriers (~10 nm). The currents

may be due to either *internal* EEE currents or SCL induced photocurrents. When the surface reaction creates electron-hole (*e-h*) pairs, hot holes may travel ballistically from the surface to the interface and traverse the Schottky barrier if the energy is larger than the barrier height  $\Phi_p$ . When photons are emitted by the surface reaction (SCL) they may be absorbed either in the space-charge layer of the semiconductor or at the Mg/Si interface.

Schottky diodes were fabricated on  $11 \times 12 \text{ mm}^2$ , *p*-type Si(111) wafer pieces with Ohmic back contacts. The Si surfaces were cleaned and hydrogen terminated in a multistep wet-chemical process using buffered hydrofluoric acid described in detail elsewhere [11]. The chemically passivated samples were transferred rapidly into the ultrahigh vacuum chamber ( $p \leq 10^{-8} \text{ Pa}$ ) where Mg layers were thermally evaporated at substrate temperatures of approximately 180 K. The thickness of the Mg films was monitored with a quartz microbalance. The diode area was  $6 \times 7 \text{ mm}^2$ . After softly approaching a front contact tip to the metal film the diode is characterized by current-voltage (*I/V*) measurements. Thermionic emission analysis [13] of the *I/V* curves yield effective Schottky barrier heights in the range between 0.60 and 0.76 eV. Using the extrapolation scheme from Ref. [13], the barrier height of the homogeneous Mg/*p*-Si(111) contact was determined from a large number of various diodes as 0.8 eV. The oxygen beam was provided by a three-stage differentially pumped molecular beam system. The chemicurrents were recorded from the diodes at zero bias and temperatures of 180 K either with lock-in techniques using a beam modulated at 121 Hz or with a pA meter upon continuous gas exposure. The gas particle flux was adjusted to  $10^{12} \text{ O}_2 \text{ molecules cm}^{-2} \text{ s}^{-1}$ . Variations of the Schottky barrier height were not found upon exposure of the diode to oxygen. Thus, the chemicurrents are not influenced by any potential barrier change as in the case of EEE.

Figure 1(b) shows three chemicurrent transients recorded at Mg/*p*-Si(111) Schottky diodes with metal

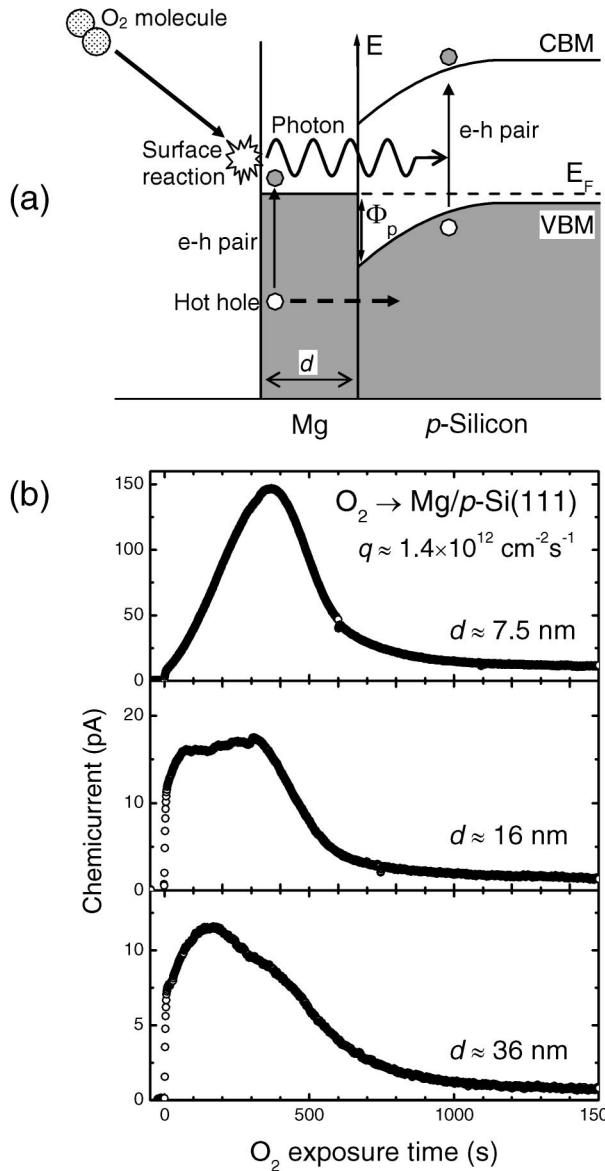


FIG. 1. (a) Principle of chemicurrent detection with Mg/*p*-Si Schottky diodes related to internal exoelectron emission and surface chemiluminescence. (b) Chemicurrent transients upon oxygen exposure with varying Mg film thickness.

film thickness of 7.5, 16 and 36 nm. For the 7.5 nm device a current trace is observed very similar to reported EEE curves [8,9] although the Schottky barrier height remains constant. The chemicurrent maximum is found at the  $O_2$  exposure time of 360 s. This finding indicates that the earlier observed EEE traces may not be exclusively explained by work function variations.

The current is attenuated with increasing Mg film thickness due to enhanced scattering of hot charge carriers in the metal. In addition, the shape of the current transients changes for Mg/Si diodes with larger film thickness. This is due to an earlier current maximum at 150 s which is less strongly attenuated than the current

maximum at 360 s. Therefore, at the 16 nm Mg/Si diode both maxima are of same magnitude resulting in a broad structure, but for the 36 nm Mg film device the earlier maximum is clearly dominating. The rapid onset of the current when the gas exposure is started is related to defects of the Mg surface. It may be enhanced by disrupting the surface prior to exposure, e.g., by preoxidation or plasma treatments.

In Fig. 2, the maximum values of many different chemicurrent traces are plotted on a semilogarithmic scale as a function of the Mg film thickness. The attenuation may be well described by an exponential relationship ( $\sim \exp[-d/\lambda]$ ). As long as the current maximum is located at the exposure time of 360 s, i.e., for Mg film thicknesses below 15 nm and at 20 nm, the attenuation constant  $\lambda$  is found to be approximately  $(5.4 \pm 1.0)$  nm, which is a typical value for attenuation of chemically induced hot charge carriers [10,11]. Above metal thicknesses of 25 nm and for the sample with 16 nm Mg film, the current maximum at 150 s dominates and is much weaker attenuated with  $\lambda = (50 \pm 15)$  nm. The Mg/*p*-Si(111) Schottky diodes were also irradiated with infrared light to compare the attenuation of the respective internal photoemission current with the chemicurrent results. For a photon energy of 0.8 eV an attenuation constant of 44 nm is determined. Therefore, the chemicurrent maximum at 150 s may be attributed to SCL induced photon absorption in the device. Because of different mean free paths of hot charge carriers and photons in Mg, the chemicurrent method allows one to distinguish EEE from SCL by changing the Mg film thickness of the device.

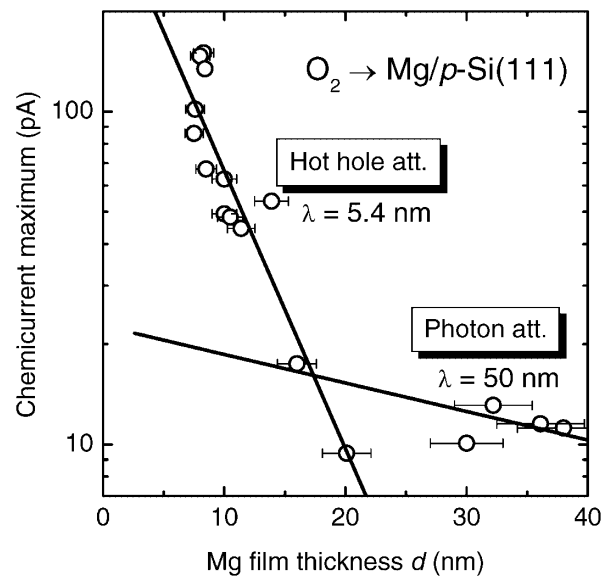


FIG. 2. Attenuation of the chemicurrent maximum with Mg film thickness. The small attenuation constant is due to hot holes created by internal EEE and the large  $\lambda$  value is attributed to SCL related photocurrents.

The internal EEE efficiency may be estimated by dividing the maximum chemicurrent in the limit of vanishing Mg film thickness ( $d \rightarrow 0$ ) from Fig. 2 by the number of oxygen molecules impinging on the diode per unit time. The calculation yields  $4.5 \times 10^{-3}$  holes per  $O_2$  particle which is 1000 times larger than typical EEE yields. This result gives direct evidence that chemicurrents measure a larger part of the hot charge carrier distribution than EEE due to Schottky barriers which are lower than the work function.

The earlier appearance of the SCL compared to the EEE maximum during oxidation of Mg surfaces has been reported before [4,14] and was interpreted in terms of work function changes which affect the EEE more directly than SCL. However, this finding is also observed at the thin-film Schottky diodes where the barrier height does not change upon exposure indicating that most likely SCL and EEE occur at different adsorption sites.

The oxygen uptake of the Mg surface was measured with Auger electron spectroscopy to demonstrate that the internal EEE currents in Fig. 1 represent the kinetics of the surface reaction. In Fig. 3 the open symbols show the peak-to-peak intensity of the  $O(KLL)$ -Auger structure at 510 eV electron energy as a function of molecular oxygen exposure. The oxygen uptake saturates for exposures above  $5 \times 10^{14} \text{ cm}^{-2}$  at a coverage of approximately 1.3 monolayers.

The solid line in Fig. 3 is the normalized integral of a chemicurrent trace recorded at a 7.5 nm Mg/ $p$ -Si(111)

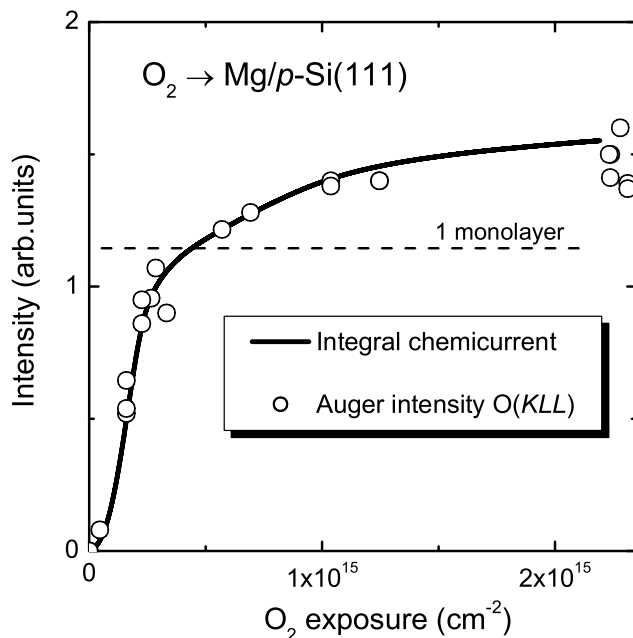


FIG. 3. Data of oxygen uptake from Auger electron spectroscopy compared to detected charge in the Mg/ $p$ -Si diodes. The film thickness was approximately 7.5 nm. The excellent agreement indicates that internal EEE currents represent the surface reaction kinetics.

diode. The integral  $\int I_{cc}(t)dt$  represents the total charge detected within the Schottky diode. Evidently, Auger and integrated chemicurrent data correspond one to one. Hence, the internal EEE currents are proportional to the reaction rate at the surface, i.e., the time derivative of the number of reactions. Since detected charge and oxygen uptake are directly proportional to each other, the probability of exciting hot charge carriers by nonadiabatic energy dissipation remains constant during  $O_2$  exposure and is independent of the oxygen coverage. For the 7.5 nm Mg/Si diode, a proportionality factor of  $5.3 \times 10^{-8}$  C per monolayer is found between detected charge and oxygen coverage. This value corresponds to the above estimated internal EEE efficiency.

The thin-film Schottky diodes can be used to monitor the chemical kinetics of the initial oxidation of Mg surfaces at low temperatures. As shown in the internal EEE current of the 7.5 nm device in Fig. 1(b), the reaction probability is initially low, but increases rapidly with increasing oxygen coverage. This behavior has been observed for oxygen interacting with various metal surfaces and was attributed to oxide island nucleation and growth [15–18]. After passing the current maximum, the reaction rate drops exponentially due to saturation of reaction sites. At 180 K, further oxidation and the formation of Mg bulk oxide is strongly inhibited.

The nucleation and growth of two-dimensional oxide islands may be described analytically in a model developed by Holloway and Hudson [17]. For oxidation of Ni(100) surfaces, they assumed that oxygen molecules impinging on the surface are physisorbed and diffuse along the surface until they desorb or reach the perimeter of a circular oxide island where the reaction is most likely to occur. The oxide growth may be controlled either by surface diffusion or the incorporation rate. In either case the time evolution of the oxygen coverage  $\Theta$  is expected to obey a simple relationship, i.e.,  $\Theta(t) = 1 - \exp[-KN_0q^2t^2]$ , where  $N_0$  is the island density,  $q$  is the molecule flux, and  $K$  is a constant including all thermodynamic parameters. The internal EEE current  $I_{cc}$  is proportional to the reaction rate and, hence, proportional to the time derivative of the surface oxygen coverage, i.e.,  $I_{cc} \propto d\Theta(t)/dt = 2KN_0q^2t \exp[-KN_0q^2t^2]$ .

In Fig. 4 experimental and model data are plotted. The solid line was calculated using a fitting parameter of  $KN_0 = 1.5 \times 10^{-30} \text{ cm}^4$  which is a reasonable value. It deviates approximately 2 orders of magnitude from  $KN_0$  values reported for the oxidation of Ni(100) surfaces at room temperature. However, the discrepancy is expected since factor  $K$  increases exponentially with decreasing temperature and the experiments at the Mg/Si diodes were performed at 180 K. The calculated data in Fig. 4 agree excellently with the measured internal EEE current. Deviations are expected for longer exposure times since the model makes reasonable predictions up to

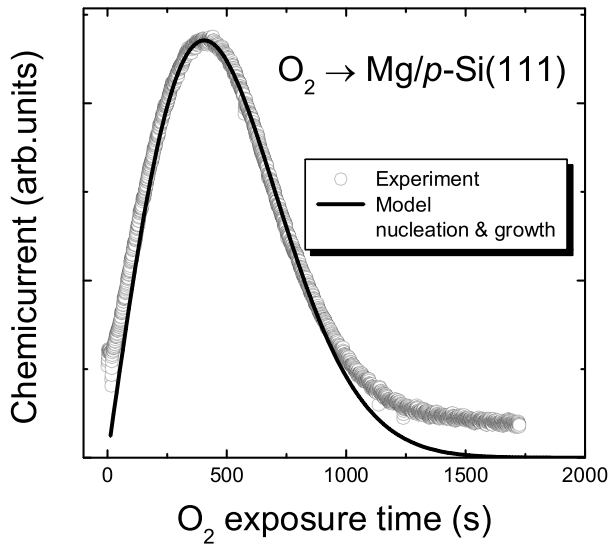


FIG. 4. Internal EEE current transients, experimental and calculated using the nucleation-and-growth model from Ref. [17].

1 monolayer only. For short exposure times the discrepancy between measured and theoretical data is due to structural surface defects which act as additional reaction centers and produce the sudden increase of the current when the exposure is started.

In summary, thin-film Mg/*p*-Si(111) Schottky diodes were used to monitor the oxidation kinetics of Mg surfaces by measuring the internal exoemission current. Since the Schottky barrier is not affected by the oxygen uptake, the current transient represents truly the time-varying reaction rate. This is confirmed by independent Auger electron measurements. If the Mg film thickness is increased photons due to surface chemiluminescence are

observed as an internal photocurrent in the diode. The chemicurrent method offers a sensitive tool to characterize surface reactions during exposures.

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