Optical response of metal–insulator–metal heterostructures and their application for the detection of chemicurrents

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Abstract. The optical response of thin-film metal–insulator–metal (MIM) systems of tantalum–tantalum oxide–Au type is studied by recording the macroscopic current across the device resulting from the low-energy electron–hole pairs excited in the metals by red and near-infrared (NIR) light ($h\nu < 2\text{ eV}$). It is observed that current flows from the top Au to the back Ta electrode, although a larger number of photons is absorbed in the latter. This directional preference is attributed to the built-in electric field across the oxide layer. The yield per photon increases strongly as photon energy becomes comparable to the barrier height. Current exhibits a strong dependence on bias voltages applied across the oxide layer. Photoyields induced by NIR light ($h\nu \sim 1.5\text{ eV}$) were found to be comparable to recently observed chemicurrents arising from exposure of a MIM sensor to atomic hydrogen, when compared on a current per photon to current per impinging hydrogen atom basis.

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1. Introduction

New applications have recently been proposed for metal–insulator and metal–semiconductor heterosystems. On the one hand, the direct conversion of chemical energy into electricity has been investigated with silicon-based titanium dioxide diodes in chemical reactors at reaction gas (CO and O₂) pressures of several 100 Torr [1, 2]. Reversing this process, such heterosystems are used to eject electrons towards the surface with the intention of stimulating chemistry [3]–[6]. On the other hand, the significance of non-adiabatic processes during surface chemical reactions [7, 8] has been studied using metal–silicon Schottky diodes [9] or metal–insulator–metal (MIM) tunnel devices [10] under ultrahigh vacuum (UHV) conditions. The detection of chemically induced currents (referred to as chemicurrents [11]) at 0 V device voltage is common to both methods. It is believed that a coupling of the motion of reactants to electronic excitation processes on the substrate surface in the course of a chemical reaction is the origin of these currents. The reactants thus dissipate a fraction of the reaction’s excess energy to the electronic system of the substrate.

MIM devices consist of a sandwich with a metal back electrode, an insulating oxide layer of a few nm thickness, which acts as a high-pass filter for carrier transport, and a metal top layer (figure 1). The band gap in the oxide defines the energy window in which transport is hindered or suppressed. Electrons excited to an energy larger than that at the bottom of the conduction band and holes at energies lower than the top of the valence band can freely traverse the oxide layer. Moreover, electrons and holes with somewhat smaller excitation energies may tunnel through the oxide barrier due to its minuscule thickness. Hence, these two fractions may be detected as a macroscopic current.
In this paper, we present an attempt to characterize the response of a MIM device to electronic excitations induced by photon irradiation with energies between $h\nu = 1.27$ and $1.95$ eV. This study is motivated by our recent use of MIM devices for the detection of chemically induced electronic excitations, for which the excitation energy is expected to be in the range of these photon energies [10]. A thorough characterization of the response of a MIM device is crucial for the interpretation of these data. MIM devices facilitate some limited spectroscopy of electronic excitations, when a bias voltage is applied between the front and back electrodes [12]. Hence, we also study the photoinduced currents when a bias voltage is present. We have chosen tantalum oxide-based MIM devices for this work because they are known to be stable up to temperatures of 480 K [13]. This type of sensor seems to be very promising for future applications in the detection of chemicurrents.

Figure 1. Upper graph: schematic view of a tantalum–tantalum oxide–gold MIM system and its band structure. Electron–electron and electron–phonon scattering in the metal as well as scattering in the built-in electric field in the oxide film are indicated. Lower graphs: density of states (DoS) of bulk Ta and bulk Au taken from [22] and [23, 24], respectively. Note the different scales of the x-axes.
Examples of surface reactions in this context are the adsorption and recombination reaction of hydrogen atoms on noble metal surfaces. The chemisorption energy of atomic hydrogen $E_{\text{ad}}$ on noble metal surfaces (Ag, Au and Cu) is smaller than 2 eV [14]–[16]. The excess energies of subsequent reactions between the adsorbed species are of similar magnitude. Thus, the maximum energy possibly dissipated to the substrate electronic system corresponds to photoexcitation by red or near-infrared (NIR) photons.

In MIM devices, photoexcitations and chemically induced excitations have particular properties that have to be accounted for:

- **Photoexcitation**
  
  * Photon energies $E_{\text{ph}}$ of red and NIR light are smaller than the band gap $E_{\text{gap}}$ in the oxide layer. Thus, photons will only be absorbed in the metallic electrode(s).
  
  * When the top metal film is only a few tens of nm thick, a significant amount of incident light is transmitted and photon absorption will also occur in the metallic back electrode, i.e. electric excitations will be created in both metal layers.
  
  * It may well be assumed that one absorption event of a photon produces one electron–hole (e–h) pair. The spectrum of the photoinduced carriers is approximated by weighting the transition probability with the density of ground state carriers below the Fermi level, $E_F$, and the density of empty states above $E_F$.

- **Chemical excitation**
  
  * Chemical processes at the vacuum interface of the top electrode will induce electronic excitations only in this vicinity.
  
  * The number of e–h pairs produced by one chemical reaction event on the surface may be larger than one. The number can only be determined if the total dissipated energy and the spectral distribution are known.
  
  * The spectrum of electronic excitations is still a subject of debate. For simple atomic adsorption processes, isotope effects that were used to infer an effective temperature have been observed [10, 17]. Various modeling efforts at different levels of sophistication suggest that the spectrum is well represented by an exponential decrease as a function of excitation energy [18]–[21]. However, this is still experimentally untested.

Hence, a direct characterization of MIM systems as a detector for chemicurrents by comparison to photocurrents seems to be inaccessible, because of selective excitation of charge carriers in the top electrode in one case and the concurrent absorption of photons in the top and back electrodes in the other case. Selective absorption of light in only the top layer of a MIM system or at the interface of a metal–insulator system may, for example, be experimentally achievable by attenuated total reflection [25, 26]. But this requires that the devices are evaporated on prisms or that a prism is brought very near ($d \approx \lambda/2$) the top electrode. The latter cannot be easily carried out in a UHV chamber as the required gap between the two surfaces of not more than 100 nm severely limits gas flow. Modern nonlinear optics using short-pulsed lasers is a promising technique to study short-lived excitations at the metal–vacuum interface. These experiments and the quantitative interpretation of the obtained data are however still challenging [27].

As we will demonstrate with the study presented here, an internal field across the oxide layer suppresses the flow of electrons from the back to the top electrode (figure 1). Hence,
Table 1. Optical absorptivities in the top Au layer (25 nm) and the Ta back electrode (20 nm) at the laser wavelengths used in this study. The last column lists the observed photocurrent normalized to the incident laser power.

| $\lambda$ (nm) | $E_{ph}$ (eV) | Abs$_{Au}$ (%) | Abs$_{Ta}$ (%) | $I_0$ ($\mu$A W$^{-1}$) |
|---------------|--------------|--------------|--------------|----------------|
| 635           | 1.95         | 3.9          | 7.7          | 99             |
| 808           | 1.53         | 2.7          | 5.4          | 20             |
| 904           | 1.37         | 2.5          | 4.4          | 4.9            |
| 980           | 1.27         | 2.2          | 3.3          | 0.87           |

in effect we have a predominant contribution from the photoelectrons created in the top electrode to the net photocurrent. This will allow us to make a meaningful comparison between photocurrents and chemicurrents.

2. Experimental

2.1. Setup

Ta films (99.99%, Mateck) (30 nm × 20 mm × 2 mm) were deposited on glass panels using an electron beam evaporator. They represent the base electrode of the device. By anodic oxidation (cyclic voltammograms up to potentials of $E = 1.7$ V), a 4 nm thick oxide film was formed on top of the Ta layer with an area of 4 mm × 2 mm. Ag strips (parallel to Ta) were deposited on the glass plate on either side of the Ta film. Afterwards, the sample was transferred to a UHV chamber, where the top Au electrode was thermally deposited. The Au film has contact with the Ag strips, which serve as conduction leads, such that a current between the top and back electrodes can be monitored. The resistivity of the top metal film was controlled during the deposition. The thickness of the Au films was determined with the help of a quartz crystal microbalance and checked afterwards by atomic force microscope (AFM) measurements. The thickness of the oxide films was additionally confirmed by X-ray photoelectron spectroscopy (XPS) sputter profile measurements.

Samples were illuminated by IR laser diodes (Thorlabs) with wavelengths 635, 808, 904 and 980 nm that delivered powers $P$ between 2 and 20 mW. (For the conversion to photon energies $h\nu$, see table 1.) The output power was carefully determined using a calibrated silicon detector (Hamamatsu SS0-BL-100-21-BNC). The laser diodes and a focusing lens were mounted on an optical bench outside the chamber. A chopper ($f = 0.5$ Hz) was placed between the sample and the light source such that the photocurrent can readily be identified even if the base line is drifting. The laser beam was directed onto the sample along the surface normal, in which case the polarization of light is irrelevant. It illuminated a spot of 1.5–2 mm diameter on the sample with a beam profile that is best approximated by a Gaussian. The photocurrents were recorded using a home-built current-to-voltage converter ($10^{10}$ V A$^{-1}$).

2.2. Barrier properties

The composition of Ta oxide layers was studied by means of XPS (Quantum 2000, Physical Instruments) using a monochromated Al K$\alpha$ x-ray source with a spot diameter of 100 $\mu$m. The take-off angle of detected photoelectrons with respect to the surface normal was 45°. The
Two caveats concerning the sputter profile measurement have to be kept in mind. Firstly, the XPS measurements were carried out at a base pressure of $10^{-9}$ mbar and in the case of the sputter profiles at a partial pressure of argon of $5 \times 10^{-8}$ mbar. The residual reactive gases in the apparatus led to an accumulation of coverage on the reactive surface between the measurement of a spectrum and the next sputter cycle. Secondly, the depth of the sputter profile was inferred from the calibrated sputter rate of $5.4 \text{ nm min}^{-1}$ in the case of a 100 nm thermal silicon oxide layer on a silicon wafer. For these two reasons, the absolute oxide thickness is difficult to ascertain. In a pragmatic approach, the depth at which the metal and the oxygen signals cross was identified with the oxide layer thickness (see the lower view graph of figure 2).

A crucial point for determining the photosensitivity in our experiments is the height and possibly the asymmetry of the internal tunnel barrier. Barrier heights of $\approx 1.7 \text{ eV}$ were already reported previously when dealing with the dielectric breakdown of the samples [13].
Figure 3. Current versus voltage plots of tantalum–tantalum oxide–Au samples recorded at $T = 50$ K. The downward arrow indicates the voltage at which the slope changes due to the onset of Fowler–Nordheim tunneling.

More detailed studies of barrier properties in Ag–TaOx–Ta devices indicated significant barrier asymmetries such that it was concluded that the barrier must be 2 eV higher at a TaOx–Ag than at a Ta–TaOx interface [28, 29].

The only method directly providing a hint on the barrier height independent of insulator thickness is the change of slope in the logarithmic current–voltage plot induced by the onset of Fowler–Nordheim tunneling [30, 31]. Figure 3 shows a current versus voltage plot recorded at $T_S = 50$ K as the devices do not withstand larger voltages at higher temperatures. In the negative voltage range (Fermi level of Ta raised with respect to that of Au), a slight change of the slope in the $\log(I)$–$U$ plot appears. This indicates that the barrier height at the oxide–Au interface is approximately 1.6 eV, which agrees quite well with the value of 1.7 eV found previously [13].

The experimental results are not so clear for the positive voltage range because no well-defined slope change can be identified when inspecting a plot of the derivative. The currents, however, are larger for this polarity with $-I(-0.5\,\text{V})/I(+0.5\,\text{V}) = 11$. In the latter case, the current must be due to electrons originating from states close to the Fermi level in the Au film. The DoS of Au at this energy is, however, only one-third that of Ta. This suggests a smaller current for positive polarity, which is the opposite of that observed experimentally. Hence, the difference in the band structure of the metals cannot explain the larger currents for negative voltages. However, one possible explanation would be an asymmetry of the tunnel barrier (see figure 1). If the barrier at the Ta–TaOx interface is only 1.0 eV, the calculated current ratio $-I_{\text{calc}}(-0.5\,\text{V})/I_{\text{calc}}(+0.5\,\text{V})$ is $\approx 10$. This interpretation is consistent with the experimental findings. It indicates a built-in electric field strength of $(1.6\,\text{V} - 1.0\,\text{V})/4\,\text{nm} = 1.5 \times 10^8\,\text{V}\,\text{m}^{-1}$ across the oxide layer, which is a value in line with that commonly reported [32].
3. Results

3.1. Photocurrent

A current in the range from 100 pA to 5 nA is observed when the MIM device (25 nm Au, 20 nm Ta) is exposed to photons with $h\nu$ in the range from 1.27 to 1.95 eV and laser powers of typically 5 mW (table 1). The current corresponds to electron flow from the top to the back electrode. It shows a marked dependence on photon energy, with the largest conversion efficiency for the shortest wavelength light. The currents were always found to vary linearly with applied laser power. For some experiments a small aperture was placed in the laser beam. A more Mexican hat-like laser beam profile can be expected for these conditions. It was observed that the current was reduced linearly with the reduced power transmitted through the aperture. With the aperture in place, only a small spot was illuminated on the Au top electrode of the MIM sensor. When this spot was moved across the sample, no significant variation of the current was observed.

3.2. Thickness dependence of the photocurrent

The photocurrent was monitored starting with a Au film of 10 nm thickness. The thickness of the Au top electrode was then stepwise increased by 2–3 nm. The observed photocurrent always flows from the top to the bottom electrode even for small Au layer thicknesses. Figure 4 shows the data as a function of top electrode thickness. A strong increase of the photocurrent (by up to a factor 20) can be observed, when the thickness of the Au top electrode is increased from 10 to

Figure 4. Observed photoinduced currents as a function of Au layer thickness for $h\nu = 1.27$ eV and a lower power of 6.7 mW (●). The black solid line serves as a guide to the eye. Calculated flux of hot charge carriers only taking electron–electron scattering into account (blue — —) and also taking electron–phonon interaction into account (red ——). The theoretical curves have been normalized with respect to the experimental data.

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Figure 5. Bias voltage dependence of photoinduced current for various photon energies recorded for a Au film of 25 nm thickness. The currents were normalized with respect to their respective values at $U_T = 0$ V. The sign of $U_T$ is defined consistent with figure 3.

25 nm. With further increasing thickness ($d > 25$ nm), the current diminishes exponentially. For thicknesses $d > 70$ nm, the currents are smaller than the noise level of 10 pA. It should be noted that these results are qualitatively similar for all photon energies studied. Moreover, experiments with the laser beam directed off-normal towards the sample surface and different polarizations showed no deviation from what is predicted by the optical properties. Thus, a contribution from an enhanced electron–phonon coupling mediated by surface electromagnetic waves [33, 34] can be ruled out for our experiment.

For Au layers thinner than 25 nm, the absorption in the Ta back electrode exceeds the absorption in the Au layer (see section 4.1.1), whereas the absorption in the Au film dominates for thicker films. Thus, it is surprising that the net photocurrent does not change sign at a Au thickness of 25 nm.

3.3. Bias dependence of the photocurrent

When a bias voltage is applied to the MIM device, a significant variation of the photocurrent is observed. Figure 5 depicts this dependence for a Au film thickness of 25 nm and the four photon energies. A polarity change is observed for all photon energies at some negative bias voltage. Obviously, the polarity change occurs for each photon energy at a specific voltage. It is noteworthy that the order of the currents normalized to its value at $U_T = 0$ V is not monotonic with the photon energy when a bias voltage is applied. The effect of the bias voltage becomes largest when the photon energy is close to but still smaller than the barrier height for electrons. For smaller photon energies, the bias voltage has less influence. It is however weakest when the photon energy is larger than the barrier height. For photon energies larger than the barrier height, current reversal happens at a bias voltage somewhat larger than −0.6 V.
We compared the influence of the bias voltages for two different Au layer thicknesses (25 and 50 nm) in order to identify whether the polarity change is induced by a stronger contribution from (i) photoelectrons from the Ta layer or (ii) photoholes from the Au layer. The photon energy of $h\nu = 1.27$ eV was chosen for this experiment since the DoS of Au is fairly flat in this region (see figure 1), leading to similar mobilities of excited electrons and holes. The absorptivities in the Ta and Au layers change from 3.1 and 3.2%, respectively, for 25 nm Au film thickness to 0.5 and 2.7% for 50 nm thickness. One would expect that a larger negative bias voltage is necessary to induce a polarity change in the case of the 50 nm Au film if indeed a stronger contribution from photoelectrons from the Ta layer is the cause, since the absorptivity in the Ta layer is reduced by a factor of 6 when compared to the situation for the thinner Au film. This is observed by the experiments as for a 50 nm Au layer the polarity does not change for bias voltages up to $-0.8$ eV. Experiments at higher voltages are not conclusive as the bias-induced tunnel current (with fluctuations of several %) then exceeds the photoinduced current, preventing an unambiguous evaluation of the photoinduced signal. Hence, the experiment suggests that the negative bias voltage results in a stronger current of photoelectrons from the back to the top electrode.

4. Discussion

4.1. Model development

For the complete characterization of photoinduced currents in heterosystems, it is necessary to

- consider the optical properties of the system treating interference properly,
- calculate the density of excited carriers in each layer and
- describe the transport rates of excited charge carriers across each medium and interface.

In this section, the transport of photoinduced carriers is treated within a three-step model: (i) excitation and relaxation processes in the metals, (ii) transport to the metal–oxide interface and (iii) tunnel transport through the oxide layer. First, we look at the optical properties of the layer system. Due to the low photon energies used ($h\nu < 2$ eV), any excitation process in the oxide layer is disregarded.

4.1.1. Optical properties. Figure 6 shows a sketch of the layer system. It consists of five media with individual thicknesses $d_i$ and four interfaces between them. Medium 5 is the vacuum from which side laser light impinges with wavelength $\lambda$. Medium 1 is the substrate carrying the three-layer MIM system. The calculation of the optical response of such a system is discussed in the appendix.

A plot of the absorptivities of the Ta back electrode and the Au top layer as a function of the thickness of the latter for different photon energies is presented in figure 7. In the absence of a Au layer (thickness = 0 nm), rather large absorptivities typical for Ta are found. For example, bulk Ta has a reflectivity of only 39% at $h\nu = 2.0$ eV. For the employed photon energies, the absorptivity of the Au layer increases monotonically up to $\approx 30$ nm film thickness, where it reaches an intermediate maximum, and finally approaches constant values of 2–3% depending on photon energy. However, the asymptotic value is practically reached for 20 nm thickness. For $h\nu = 1.95$ eV, the increase continues longer and the asymptotic value of 4.5% is reached for a thickness $d \approx 60$ nm. These asymptotic values correspond to the values for bulk Au absorption.
Figure 6. Layer and interface assignment in the MIM multilayer system. Media 1 and 5 (glass and vacuum) are considered as half-spaces with \( d_1 = d_5 = \infty \).

Figure 7. Absorptivities of the Ta \((d = 20 \text{ nm})\) and the Au layers with a 4 nm oxide layer separating these in a MIM system. The angle of incidence is assumed to be 0°.

which are given by the reflectivity at the Au–vacuum interface. Experiments for a 20 nm thick Au film evaporated on glass show 5% absorption for similar photon energies [35, 36]. It should be noted that these calculations are based on the bulk values of the optical constants. The values given can be expected to be questionable for Au film thicknesses \( d < 10 \text{ nm} \). In this regime, the Au films become discontinuous and the optical constants for thin films differ significantly from their bulk values [37]–[39].
4.1.2. Excitation in metals. The number of e–h pairs \( N_{e-h,i} \) generated per unit time in each layer \( i \) is calculated from the absorptivities (difference of the Poynting vectors at the layer interfaces \( q_i - q_{i-1} \)) of the nascent distribution of \( E_F < E < E_F + h\nu \) and be spatially spread along the coordinate into the bulk \( z \). The integral over their distribution function \( G(E, z) \) has to equal \( N_{e-h,i} \).

Next we want to derive this distribution. We start with a description of the nascent distribution of excited electrons and holes \( F(E) \)—neglecting subsequent relaxation processes—as a function of their respective energy \( E \) at a temperature \( T \) and add the spatial aspect later. We use as DOS \( g(E) \) that of a free electron gas \((\sim \sqrt{E})\), as we found that using the distribution shown in figure 1 does not lead to significantly different results. The nascent distribution of excitations can be expressed as

\[
F(E) = \theta \cdot g(E - h\nu) \cdot f(E' - h\nu, T) \cdot \left[ 1 - f(E', T) \right] \\
- \theta \cdot g(E) \cdot f(E', T) \cdot \left[ 1 - f(E' + h\nu, T) \right],
\]

where \( g(E) \) is the DoS and \( f(E', T) \) represents the Fermi function with \( E' = E - E_F \). \( \theta \) is the fraction of electrons excited by laser light. The first summand describes deviation from the ground state distribution due to promotion of electrons to states at energy \( E \), and the second term describes depletion by the creation of holes due to promotion of electrons to energy \( E + h\nu \). We neglect the change of the density of final states because its variation is small. Obviously, this equation is only applicable if \( \theta \) is small such that the ground state distribution is not depleted nor is the excited state saturated. As will be seen below, this condition is fulfilled under the conditions of the experiments presented here.

Because we use cw light, a steady-state distribution will arise for which excitation processes and relaxation processes balance. This nascent e–h distribution, \( F(E) \), multiplied by a decay rate \( \gamma(E) \) of the excited carriers and the volume of the irradiated electrode gives the number of relaxation events. In the steady state, it must be equal to the number of excitation events (i.e. absorption events of photons \( \equiv N_{e-h,i} \)). Several processes contribute to the decay rate of excited charge carriers, namely e–e and e–ph scattering processes. These processes are characterized by their respective mean free path lengths \( \lambda_{e-e} \) and \( \lambda_{e-ph} \), which have been intensively studied \([42]–[48]\).

The energy dependence of the e–e scattering length \( \lambda_{e-e}(E) \) is described as in \([49]\) as

\[
\lambda_{e-e}(E) = 4 \ a_0 \ (1 + r_s) \ \frac{|E - E_F|}{E_F} \ \left[ \frac{|E - E_F|}{E_F} - 1 \right]^{-2},
\]

where \( a_0 \) is Bohr’s radius and \( r_s \) is the mean radius of a conduction band electron. Absolute values of the excess energy \( E - E_F \) are used such that the mean free paths for electrons and holes are identical if they have the same energy with respect to the Fermi level. Division of the carrier velocity \( \sqrt{2 \cdot E/\hbar} \) by \( \lambda_{e-e}(E) \) gives the scattering rate

\[
\gamma_{e-e}(E) = \sqrt{2 \cdot E/m} \ \left[ \lambda_{e-e}(E) \right]^{-1}.
\]

It is also necessary to consider e–ph scattering. In thin films, e–ph scattering can be considerably enhanced by grain boundaries, which partially lift the requirement of the

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conservation of momentum [50]. In this work, the room temperature value from [42, 48] is combined with the energy dependence reported in [51], leading to

$$\gamma_{\text{e-p}}(E) = B \cdot T \cdot \sqrt{\frac{E + E_F}{E_F}}$$  \hspace{1cm} (5)

with $B = 1.23 \times 10^{11} \text{K}^{-1} \text{s}^{-1}$.

Another scattering effect can play a role due to the grain structure of the film. Grain sizes of noble metal films are known to scale linearly with film thickness [52, 53]. Consistently, we find that the typical grain diameter of our Au films is around 20 nm for a 25 nm thick film [54]. The grain boundaries are known to have low transmission for electrons [55, 56]. Then, this value, 20 nm, may be an upper limit for the mean free path to be expected in our experiments. Hence, an additional energy and temperature-independent scattering rate due to grain boundary scattering $\gamma_{\text{gb}}$ is added. The total scattering rate $\gamma_{\text{total}}(E)$ is then the sum of the different scattering rates:

$$\gamma_{\text{total}}(E) = \gamma_{\text{e-e}}(E) + \gamma_{\text{e-ph}}(E) + \gamma_{\text{gb}}.$$  \hspace{1cm} (6)

The nascent spatial distribution of photoexcited e–h pairs, $G(E, z)$, is proportional to the differential absorptivity in metal films (figure 8). The proportionality to $e^{-k_{\text{opt}} z}$ is used to derive the spatial carrier distribution according to Lambert’s law

$$G(E, z) \propto e^{-k_{\text{opt}} z},$$  \hspace{1cm} (7)

where $k_{\text{opt}} = \frac{\ln(q_4/q_3)}{z_4 - z_3}$. In the bottom electrode $G(E, z)$ is similarly proportional to $e^{-k_{\text{opt}} z}$. At each point along $z$, the energy dependence is given by $F(E)$, such that we obtain

$$G(E, z) = C \cdot F(E) \cdot e^{-k_{\text{opt}} z}.$$  \hspace{1cm} (8)

To determine the unknown constant $C$, one has to solve

$$\int_{z_i}^{z_{i+1}} \gamma(E) \cdot V \cdot G(E, z) \, dz = N_{\text{e-h,i}},$$  \hspace{1cm} (9)

where $V$ is the irradiated volume. Under the experimental conditions chosen here, $G(E, z)$ varies slowly with $z$ because the penetration depth is comparable to the film thickness.

At this point it is possible to calculate the density of excitations in the Au film. The irradiated surface area is 2 mm $\times$ 2 mm and the thickness of the film is e.g. 20 nm, resulting
in an irradiated volume $V$ of $8 \times 10^{-14}$ m$^{-3}$. From (1), one obtains $N_{e-h,i} = 1.5 \times 10^{15}$ s$^{-1}$. Solving

$$\int_{E_F}^{\infty} F(E) \cdot \gamma(E) \cdot V \, dE = 1.5 \times 10^{15} \text{ s}^{-1},$$

one arrives at $\theta = 1.2 \times 10^{-16}$. Using this value in (2) yields the carrier distribution $F(E)$ shown in figure 9. A significant broadening of the photoexcited distribution at its high-energy edges even for $T = 300$ K is worth noting. Close to the Fermi level, $F(E)$ decreases because the density of electrons below $E_F$ is already reduced and states above $E_F$ are already thermally populated. The density of excited electrons corresponds to $\approx 2 \times 10^{16}$ cm$^{-3}$, which is very low when compared to experiments using pulsed lasers and thin Au films, in which case excited carrier densities of some $10^{20}$ cm$^{-3}$ result [57].

4.1.3. Transport to the interfaces. Next we want to derive the distribution of carriers arriving at the interfaces resulting from the transport of excited carriers through the metal films. Transport of photoexcited carriers in thin metal films and subsequent transport over a barrier have been discussed in several reports applying one-dimensional (1D) [46, 58] and 3D models [45, 59]. These transport models consider e–e and e–ph interactions and free flight between these events. Processes where several e–ph scattering events occur between two e–e scattering events are very unlikely. Hence, any redirection of electrons that are originally traveling inclined versus the interface normal towards a direction normal to the oxide interface is disregarded. Additionally, electrons are considered as lost after one e–e scattering event, i.e. only electrons arriving with their primary energy at the interface are considered. Secondary electrons are neglected.

We start with the nascent distribution $G(E, z)$ according to (8). The transport is described by a 1D model considering the distances $z - z_3$ and $z_2 - z$ to the inner interfaces leading to weighting factors of $\exp\left[-\frac{(z_2 - z)}{\lambda(E)}\right]$ and $\exp\left[-\frac{(z - z_3)}{\lambda(E)}\right]$ due to the limited free path lengths of the carriers. Thus, the carrier distributions, $H(E)$, arriving at the front and back of the oxide layer can be represented by

$$H(E) = \int_{z_3}^{z_4} G(E, z) \, e^{-\frac{(z - z_3)}{\lambda(E)}} \, dz$$

and

$$\int_{z_1}^{z_2} G(E, z) \, e^{-\frac{(z_2 - z)}{\lambda(E)}} \, dz,$$

respectively.

$H(E)$ at the Au–TaOx interface and $F(E)$ are compared in figure 9 for the photoexcitation of a 25 nm thick Au film with $\hbar \nu = 1.37$ eV. The values for $\theta$ and $C$ were derived by solving the equations given above. Evaluating $\int H/E \, dE$ in figure 9 indicates a ratio of 73% reflecting the loss processes. In particular, the scattering significantly reduces the number of higher-energy electrons and holes arriving at the interface when compared to the nascent distribution. $H(E)$ represents the number and distribution of carriers, which are to be considered for the next step, namely the tunnel process through the oxide barrier.
4.1.4. Transport through the oxide. Tunneling processes may contribute significantly to the transport of excited charge carriers as the oxide layer is thin. Tunnel processes across insulating layers comprise electron as well as hole tunneling. For Ta oxide the band gap $E_{\text{gap}}$ is about 4 eV [60]. The barrier for electrons and holes differs only by about 0.8 eV. For that reason electron and hole tunneling must be considered to obtain a proper description of the transport. This is done using a simplified two-band approach by evaluating the dispersion relation of the tunneling electron to

$$k(E) = \sqrt{\frac{2 \cdot m}{\hbar^2} \cdot \frac{(E - E_{\text{CB}}) \cdot (E - E_{\text{VB}})}{E_{\text{g}}}}.$$  

(12)

The tunnel probability $W(E)$ is evaluated by

$$W(E) = \exp \left[-2 \cdot \int_0^d \text{Im}(k) \, dx\right],$$

(13)

where $d$ is the oxide layer thickness.

Spectra of tunneled electrons are derived by building the product $H(E) \cdot W(E)$. The current across the oxide resulting from excited carriers is calculated as

$$I_{\text{calc}} = \int \overline{\gamma} \, H(E) \cdot W(E) \, dE,$$

(14)

where the mean relaxation rate $\overline{\gamma}$ serves for normalization purposes [61]. We have finally arrived at an expression for the observable photocurrent.

4.2. Comparison to experiment

We have observed that as long as no bias voltage is applied, the current always flows from the top to the back electrode regardless of Au film thickness. This finding appears to be in conflict.
with the calculated absorption in the metal layers, which is smaller for the Au layer as long as it is thinner than \( \sim 25 \) nm (table A.1). This finding indicates that photoelectrons excited in the Ta back electrode contribute insignificantly to the net photocurrent, albeit the larger fraction of the light is absorbed there.

As the barrier for holes is larger by 1 \( \text{eV} \), it may be expected that holes contribute little to the observed current at least for the smaller photon energies. A conceivable mechanism giving rise to a dominant contribution from the top electrode excited electron to the photocurrent is the scattering of photoexcited carriers in the conduction band of the oxide when a built-in electric field is present in the oxide [32, 62, 63]. Electron–electron scattering processes in the oxide can be neglected due to the low carrier density. e–ph scattering, which is dominant in the oxide, causes energy losses of \( \approx 100 \text{ meV} \) [64, 65]. It should be noted that e–ph scattering causes a larger energy loss in oxides than in metals, since in oxides scattering with optical phonons dominates whereas acoustical phonons are the main scatterers in metals. These energy losses hamper the transport of electrons traveling against the built-in field (see the broken line in the upper view graph of figure 1). The energy loss connected with a scattering event leads to a drastically decreased tunnel probability as these electrons now have to tunnel through a thicker layer. For electrons that travel from the top to the bottom electrode, this does not matter, since they already passed the maximum of the barrier (see the solid line pathway in figure 1). But for electrons traveling from the bottom to the top electrode, the diminished tunnel probability reduces the overall transport rate in this direction decisively.

Hence, the built-in field provides a natural explanation for a strong attenuation of the flux of electrons traveling from the Ta to the Au layer with energies in the vicinity of the height of the barrier. However, this ‘directional effect’ of the oxide’s internal field will only be operative when the mean free path for e–ph scattering in the oxide is in the range of or smaller than the oxide thickness. This seems to be the case as values of 0.4–0.6 nm for the mean free path were reported [66]–[68].

A smaller contribution to the same net effect arises from a difference in the band structures of the two metals (see figure 1). Ta has two maxima in the DoS at 0.5 and 1.3 eV below the Fermi level. If we make the simplifying assumption that the excitation rate is proportional to the DoS, one would expect that excited electrons with excess energies of \( h\nu - 0.5 \text{ eV} \) and \( h\nu - 1.3 \text{ eV} \) are most abundant. In contrast, following this simple argument the smooth DoS of Au would lead to more homogeneous excited carrier distributions with excess energies up to \( h\nu \). Thus, the probability of exciting an electron to \( h\nu \) with respect to the Fermi level is larger in Au than in Ta. These electrons should dominate the net current, when \( h\nu \) is close to the barrier height.

Hence, we consider in further modeling only the electron flux from the top to the back electrode, neglecting partial currents in the opposite direction. The much larger barrier for hole transport causes it to be marginal such that we also neglect this current in the further discussion. Figure 4 presents the calculated current as a function of Au layer thickness for \( h\nu = 1.27 \text{ eV} \). The functional form of the dependence is well reproduced. A maximum appears at 8 nm Au film thickness followed by a monotonic decrease to 2% of the maximal value at \( d = 70 \) nm. But two discrepancies are obvious:

1. The position of the calculated maximum is at too small a thickness when compared with the experimentally observed one.
2. The experimental currents decrease more rapidly than our model predicts; the observed signal decays to zero at \( d = 50 \) nm, whereas the theoretical value shows only a decrease to 40%.

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Scattering processes also influence the transport of photoelectrons in metals. A rather large loss of excess energy is induced by e–e scattering. The mean energy \( E'' \) after e–e scattering for an electron with initial energy \( E' = E_F + 1.5 \text{ eV} \) has a value of \( E'' \approx E_F + 0.4 \text{ eV} \) (as indicated in the upper view graph of figure 1) [69, 70]. Hence, photoelectrons will not contribute to the photocurrent once they have encountered a single e–e scattering event.

This is not the case for e–ph scattering in metals, in which case only 10 meV is exchanged [71]. Hence, even after an e–ph scattering event these electrons must be considered as carriers that are still able to tunnel through the oxide barrier with a nearly unchanged probability. There are numerous calculations for the photosensitivity of metal–semiconductor devices considering both scattering processes [46, 58, 72]. However, simple analytical solutions for transport over a barrier are only achievable for metal–semiconductor devices with a sharp cut-off energy [72], which is not the case for MIM systems with nm thick oxide layers.

The influence of e–ph scattering can be seen when comparing the curves in figure 4. The predicted maximum shifts to 10 nm when one takes e–ph scattering according to (5) and (6) into account. Hence, we conclude that the mismatch of the position of the maximum must be due to shortcomings of the model. In the experiment, the thickness of the Au layer will not be uniform and thinner areas may contribute predominantly to the current. On the model side, the rigorous neglect of a back current may explain the discrepancy. Moreover, one can expect a reduced mean free path since the Au film is polycrystalline.

The difference in the position of the maximum may also be due to a deviation of the optical constants for \( d < 20 \text{ nm} \) from the bulk values being used in the calculations. This suggestion may be experimentally tested by \textit{in situ} ellipsometric studies of the optical properties during film growth as performed in [73], which is however beyond the scope of this work.

In order to make further contact with the experiment, we calculate

\[
Y_{\text{photo}} = \frac{I_{\text{calc}}}{e \cdot N_{e-h, 4}}
\]

as the photoinduced current yield. Figure 10 shows a comparison of the calculated yields with the experimental ones. As can be seen, the agreement in the trend is excellent, although the experimental yields are about an order of magnitude smaller. Closer inspection shows that the difference is a factor of about 5 at the lowest photon energy and a factor of 12 at the highest one. This difference is likely due to a scattering process not accounted for in the model as reflection from the Au–TaOx interface, or the 1D simplification of our model. It may however be concluded that our model based on the bulk values for optical properties of the Au film, the experimentally determined barrier properties (current voltage plots in figure 3 and the sputter profile in figure 2) and 1D transport describes the optical response of the layered system reasonably well.

4.3. Spectroscopy

Applying a negative bias voltage across the oxide layer results in (i) a reduction of the current and (ii) a reversal of direction at a larger voltage. It is remarkable that for \( h\nu \) smaller than the barrier height, a stronger dependence is observed than for \( h\nu = 1.95 \text{ eV} \). In the latter case, the current reverses only for a substantial bias voltage (\( -U_T > 0.6 \text{ eV} \)). According to the interpretation of the current–voltage plots (see figure 3), this photon energy is larger than the barrier height at the TaOx–Au interface. Hence, a partial compensation of the built-in field has little influence on the current. However, at \(-0.6 \text{ V} \), the built-in field is largely compensated and
photoelectrons created in the tantalum back electrode become the dominant contribution to the photocurrent.

For the smaller photon energies ($h\nu = 1.27, 1.37$ and $1.53$ eV), the voltage at which the current reverses is smaller when the photon energy is closer to the barrier height. That is, the reversal is observed at smaller voltages for larger photon energies. Moreover, the dependence on bias voltage is more pronounced. The photoelectrons have to tunnel for these photoenergies. Hence, the bias voltage has a stronger effect. Electrons excited in the Ta layer with energies close to the top edge of the tunnel barrier are most strongly influenced. A bias of $-0.2$ V is sufficient to induce a polarity change of the photocurrent for $h\nu = 1.53$ eV. The influence of the bias voltage then becomes weaker for further decreasing photoenergies. For $h\nu = 1.27$ eV, already $-0.4$ V is necessary to induce a polarity change.

Hence, this experiment supports the fact that at zero bias the built-in field in the oxide results in a directional preference for the current such that the net photocurrent observed is always dominated by photoelectrons excited in the top Au electrode. This interpretation seems to hold for Au layer thicknesses between 15 and 70 nm, whereas photoelectron origination from the Ta electrode may play a role for Au thicknesses $d < 25$ nm and for simultaneously applied positive bias voltages. As the smallest photon energy studied is still larger than the barrier height for electrons on the Ta–TaOx interface side, this argument may well also hold for photon energies between 1.27 and 1.53 eV.

4.4. Comparison of chemical and photoinduced energy dissipation

Ta–TaOx-based devices can also be used to study chemically induced electronic excitations [10] using e.g. an atomic hydrogen beam. We want to compare these two different excitation sources by the evaluation of their yields. The source for the chemically induced excitation is located at the outer surface of the top electrode. There are no chemically induced excited carriers from the bottom electrode. Hence, we use for the comparison a bias voltage of 0 V. In this case,
the photocurrent is also dominated by carriers from the top electrode. A thickness of 15 nm is chosen for this comparison. Photoexperiments are possible with film thicknesses as small as 9 nm. But experiments with the atomic hydrogen source were found to be unreliable for such a thin top electrode as the current–voltage plots of the device immediately changed because of the exposure to atomic hydrogen. The latter might be caused by doping of the oxide as the grain structure of the metal film may allow rapid permeation by hydrogen. Thus, the incoming atoms find a path to the oxide. But the current–voltage plots are stable for Au thicknesses >15 nm under hydrogen exposure.

We define the yield for the chemicurrent as

\[ Y_{\text{chem}} = \frac{I_{\text{chem}}}{e \cdot j_H}, \]  

(16)

where \( j_H \) is the incident flux of hydrogen atoms impinging on the sample surface. A yield of \( 3 \times 10^{-5} \) was reported in [10]. For a Au film thickness of 15 nm, a yield of the same order is observed for \( h\nu = 1.53 \text{ eV} \).

However, this simple comparison neglects any details that make these processes different as discussed in the introduction, namely that (i) photon absorption occurs over the whole film depth whereas chemically induced excitations are only created at the outer surface, and (ii) photon excitation nearly evenly populates states, whereas theoretical modeling indicates that the chemically induced excitations are characterized by a distribution that rapidly falls off at higher energies. The latter is consistently found regardless of the different theoretical concepts employed, time-dependent density function theory [74], application of the Newns–Anderson model [19, 75] or perturbative approaches [21, 76].

In view of these factors which suggest that the chemically excited excitations about 1.5 eV are more strongly attenuated as they, on average, have a longer path, and are less abundant when compared to photoexcitation, the similar yield is surprising. However, it may be of importance that the chemically induced current does not compete against any current from the back electrode to the top. It may be safe to conclude that the data presented in this paper suggest that the reported chemicurrents arise from excitations to energies around the height of the barrier at the TaOx–Au interface, namely 1.4–1.9 eV. It will take further work to quantitatively understand the size of the chemicurrent.

5. Conclusion

Photocurrents in Ta–TaOx–Au systems were investigated experimentally for various photon energies and top electrode thicknesses. The current flows always from the top to the back electrode, contrary to what is expected based on the absorptivities of the two layers. Complementary calculations taking into account reflection at the four interfaces and interference effects in the layers indicate a dominant excitation of photoelectrons in the Ta bottom electrode for Au layer thicknesses \( d < 25 \text{ nm} \). Only for thicker Au films with \( d > 35 \text{ nm} \) can photoelectrons in the top electrode be expected to be more abundant for all photon energies studied here.

This finding reveals a significant influence of the internal electric field across the oxide film, which attenuates the photocurrent contribution from the Ta bottom electrode. A negative bias voltage can be applied which cancels the built-in electric field. Under these conditions, indeed a reversal of the current is observed.
A simple 1D model was proposed for calculating the photocurrent yield. The tunnel processes through the oxide layer are accounted for in a two-band model. This model predicts the observed sharp rise of the photoyield with photon energy well, but overestimates the absolute magnitude because it neglects, among other details, the scattering at the interfaces.

The experimental current shows a marked maximum at a Au layer thickness of 25 nm. For layer thicknesses larger than 60 nm, the current has largely vanished. A similar dependence is predicted by the model, which however underestimates the thickness at which the maximum occurs.

The yield—the current per elementary event—in the chemicurrent experiment, where a MIM sensor was exposed to a flux of H-atoms, is of the same order of magnitude as the yield observed for photocurrents at $h\nu \sim 1.5$ eV. The photoyield for $h\nu = 1.95$ eV is an order of magnitude larger than the observed chemicurrent yield. This finding suggests that the chemicurrent arises from hot carriers with energies well below 1.9 eV and likely also below the barrier height at the Au–TaOx interface.

It is worth noting that it is conceivable to observe a chemicurrent even if the distribution of excitations extends only to an energy 0.3 eV smaller than the barrier height, as we could report a photocurrent for this situation.

In summary, we suggest that the response of MIM sensors to surface electronic excitations can indeed be characterized by optical experiments. We are confident that our description of the response of such devices to photon irradiation for excitation energies similar to or smaller than the internal barrier enables unprecedented insights into their physics and improves significantly over what has been done for higher excitation energies [12]. This is a prerequisite in order to interpret the data obtained when these sensors are used to detect the energy dissipation into electronic degrees of freedom of the substrate during chemical reaction. Further progress in modeling will require a Monte Carlo approach to the carrier dynamics and the results are awaited with great anticipation.

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Appendix

In this appendix, we detail the calculation of the optical properties of the MIM layer system. Electric field vectors above an interface are always denoted as $A$, below an interface with $B$. The notation is similar to that used by Edwards [41]. The index numbers the interface. Further, the letter index $m$ denotes the direction downwards (direction of incident light) whereas $p$ assigns the direction upwards (direction of reflected light). $A^p_i$ denotes the field vector above interface $i$ in the upward direction. The angle of incidence of light in each medium is denoted as $\phi_i$ and measured against the normal of the respective interface.

The field vectors at each interface can be determined from two equations:

$$A^p_i = r_{ij} \cdot A^m_j + t_{ij} \cdot B^p_i,$$  \hspace{1cm} (A.1)

$$B^m_i = r_{ij} \cdot B^p_j + t_{ij} \cdot A^m_j.$$  \hspace{1cm} (A.2)

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Table A.1. Optical constants used in this paper. For the TaOx layer, $k = 0$ is assumed.

| $h\nu$ (eV) | $n$ (Ta) | $k$ (Ta) | $n$ (TaOx) | $n$ (Au) | $k$ (Au) |
|-------------|----------|----------|------------|----------|----------|
| 1.95        | 1.20     | 3.20     | 1.8        | 0.142    | 3.37     |
| 1.53        | 1.34     | 3.64     | 1.8        | 0.149    | 4.65     |
| 1.37        | 1.32     | 4.00     | 1.8        | 0.166    | 5.34     |
| 1.27        | 1.30     | 4.42     | 1.8        | 0.179    | 6.04     |

The reflectivities between media $i$ and $j$ are denoted as $r_{i,j}$, and the corresponding transmissivities as $t_{i,j}$. They are given by the Fresnel equations

\[ r_{i,j} = \frac{n_j \cdot \cos(\phi_i) - n_i \cdot \cos(\phi_j)}{n_j \cdot \cos(\phi_i) + n_i \cdot \cos(\phi_j)}, \quad (A.3) \]
\[ t_{i,j} = \frac{2 \cdot n_i \cdot \cos(\phi_j)}{n_j \cdot \cos(\phi_i) + n_i \cdot \cos(\phi_j)}, \quad (A.4) \]

where the $n_i$ represent the complex index of reflection (table A.1). The upward and downward transmissivities through a medium $i$ are

\[ B_i^p = m_i \cdot A_{i-1}^p, \quad (A.5) \]
\[ A_{i-1}^m = m_i \cdot B_i^m. \quad (A.6) \]

In (A.5) and (A.6) the transmissivities are given by

\[ m_i = \exp(-I \cdot n_i \cdot \cos(\phi_i) \cdot 2 \cdot \pi \cdot d_i \cdot \lambda), \quad (A.7) \]

where $I = \sqrt{-1}$.

Since (A.7) describes the transmission through one medium $i$, all variables carry the same index $i$. For a system with $n$ interfaces, one has $4n$ unknowns $A_i^m$, $A_i^p$, $B_i^m$, $B_i^p$, but $4n - 2$ equations. The two missing equations can be derived simply.

The incoming field vector $A_4^m$ (see figure 6) is known experimentally and set to 1 for the purpose of this calculation:

\[ A_4^m = 1. \quad (A.8) \]

It is further assumed that no light hits the sample from the backward direction through medium 1:

\[ B_1^p = 0. \quad (A.9) \]

With equations (A.1)–(A.9), one can derive a $4 \cdot n - 2$ dimensional matrix that completely determines the optical properties of the layer system.

The Poynting vectors $q_{i}^{a}$ above and $q_{i}^{b}$ below the $i$th interface are calculated and the differences $q_{i+1}^{a} - q_{i}^{a}$ (and $q_{i+1}^{b} - q_{i}^{b}$ as a crosscheck) are taken as the absorptivity of the $i$th medium. Thus, we denote with the term absorptivity the fractional amount of light absorbed in the particular medium integrated over its thickness.
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