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Laser Effects on Volta Potential Transients Recorded by a Kelvin Probe

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A laser beam focused beneath a Kelvin probe needle allows for evaluation of laser-induced Volta potential shifts that can be used to identify (ir)reversible structural rearrangements at the sample surface. This work investigates the impact of laser irradiation on different substrate materials and the influence of laser power and wavelength to explore possible additional areas of analytical applications. Complete and instantaneous potential recovery was achieved with a 785 nm beam, whereas inverse and less meaningful potential shifts result for highly reflective Si wafers. Moreover, similarities to photovoltage transients recorded on solar cell devices are discussed.

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A combined Kelvin probe (KP) and Raman spectroscopy approach was previously introduced for spectroelectrochemical surface analysis.[1,2] A 532 nm laser beam with probing area partly placed beneath the KP needle allows the collection of Raman spectra. Photons scattered at the sample surface influence the electrical properties of the KP plate capacitor formed by the needle tip, the sample surface, and the air gap in between. Convoluted laser-induced processes at the needle and/or sample surface possibly involve drying, adsorption/desorption of organic contaminants, photoelectric effects, and structural rearrangement of crystalline phases.[1,2] The decrease in Volta potentials observed for laser-exposed bare steel never fully relaxed back to the initial state, while those for hematite (α-Fe_2O_3)-covered steel immediately recovered after laser exposure.[1] Recovery kinetics were strongly dependent on relative humidity but also reminiscent of photovoltage transients observed with ZnO or TiO_2 films deposited on Si wafers and solar cell devices.[1,3–5]

To explore contributions from photovoltage and to check whether reversible and minimized laser-induced Volta potential changes can be detected with the KP, in this work transients resulting from sample exposure to 785 nm laser beams of varying power are compared to those previously observed with a 532 nm laser. Steel, macroscopic hematite layers on steel as well as ZnO and Si substrates are investigated to further assess the applicability of a KP for sophisticated spectroelectrochemical in situ approaches.

Experimental

A Raman laser probe was built in the sample chamber of a custom-made KP from the Max-Planck-Institute for Iron Research (Düsseldorf, Germany) (Fig. 1).[1,2] The distance between the 500 μm diameter KP needle and the sample surface was continuously monitored. Volta potential measurements were performed in humid air (RH $\geq$ 80%) at ambient temperature. A continuous wave (CW) 785 nm multimode laser source (PI-ECL-785-300-SH, Process Instruments) was coupled to a fiber optic probe (RP785/12-5, InPhotonics; 7.5 mm focal length, 135 μm beam diameter at the focal spot) that focused a beam on a probing area partly beneath the KP needle at an angle of ~50°.

As-received 1018 steel sheets (1388K15, McMaster-Carr) were ultrasonicated in acetone prior to laser exposure. Macroscopic hematite layers were prepared by annealing clean steel coupons in a muffle furnace (550-14 Isotemp, Fisher Scientific) for 5 h at 600°C in air.[1,6] Zinc foil was purchased from Goodfellow (ZN00301; 99.95+ %, 0.2 mm thick) and annealed for 4 h at 300°C in air to form a covering ZnO film. Pieces of Si(100) wafers from Si-Tech Inc. (62729961; 50–65 Ω) were used following successive ultrasonication in acetone and methanol.

Results and Discussion

Fig. 1 presents a Volta potential transient recorded on bare steel. After 5 min, a 785 nm laser beam was switched on and focused beneath the KP needle so that partial overlap between the area probed by the KP and that irradiated by the laser was achieved.[1] Similar to previous observations made with a CW 532 nm beam, an instantaneous reduction of the potential of ~40–50 mV resulted, whereas the signal describing the separation distance between the sample and KP tip remained unchanged.[1] The distance monitoring for the employed KP is based on a sensitive potential measurement by an electric circuit and it was shown that this constant distance signal indicates that the

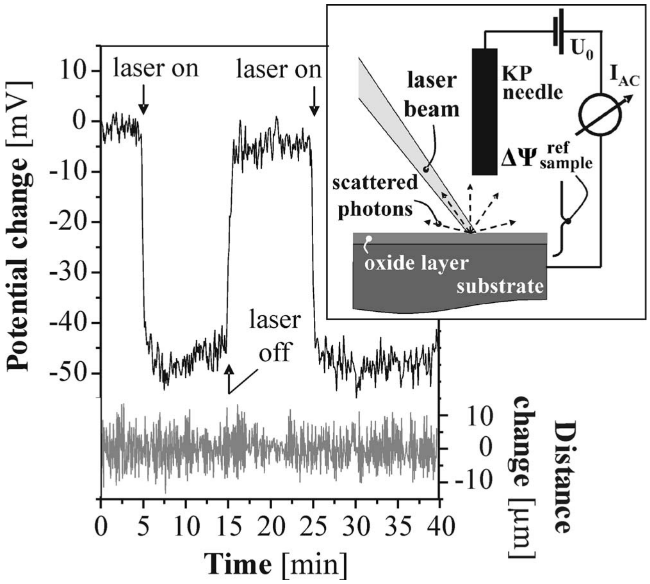

Figure 1. Potential and distance transients recorded on bare steel irradiated with a 785 nm laser beam (output energy: 100 mW) focused beneath the KP needle. Upper right corner: Schematic illustration of the experimental setup.[1,2]

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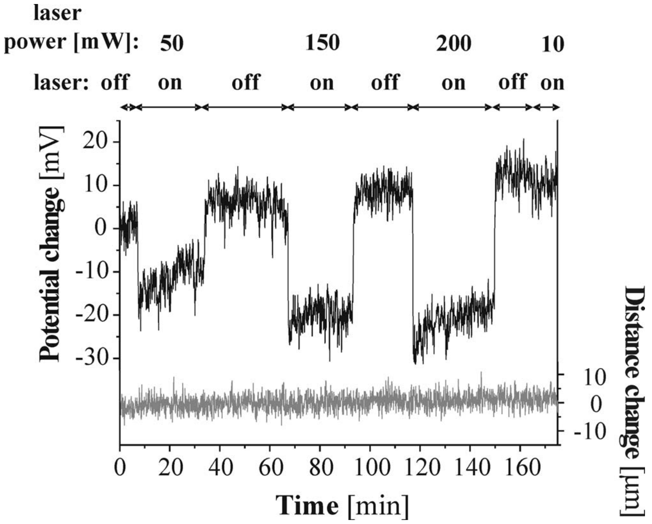

Figure 2. Potential and distance transients recorded on hematite-covered steel irradiated with a 785 nm laser beam focused beneath the KP needle and operated at output energies between 10 mW and 200 mW.

KP needle was not placed directly in the laser beam path although photons reflected at the sample surface may hit the needle.[1] At t = 15 min, the laser was turned off and the potential immediately recovered. This was not observed when a CW 532 nm beam was used, for which irreversible potential changes were correlated to the formation of hematite on the substrate surface.[1] A CW 632.8 nm laser also did not induce such crystalline rearrangement[1] and Fig. 1 now confirms that potential shifts are fully reversible even after several light on-off cycles if the laser wavelength is long enough.

Fig. 2 shows equivalent potential transients recorded on steel covered with a macroscopic layer of hematite. Complete and instantaneous potential recovery is observed independent of the energy output of the 785 nm laser. Very small potential changes are detectable at 10 mW (<5 mV), whereas increasingly larger changes are observed at higher laser power outputs (~15, 25 and 30 mV at 50, 150 and 200 mW, respectively). The absolute values should not be directly compared to those detected on bare steel due to possibly varying overlaps between laser irradiated and KP probed substrate areas. However, the observed trends are reproducible and meaningful because Fig. 2 clearly shows a non-linear dependence between laser power output and KP potential shifts. This means that light-induced deviations of Volta potentials detected, e.g. while Raman spectra are recorded, can be effectively minimized with reduced laser power. Moreover, if higher energy output is required, the absolute value of inevitable potential shifts that have to be taken into account seems to be limited.

In contrast to experiments performed with a 532 nm laser on α-Fe_2O_3, irradiation with 785 nm (i.e., ~1.6 eV) laser light should not exceed the bandgap of hematite (typically, $E_g \approx 2.2$ eV[7]). It suggests that the instantaneous recovery of laser-induced KP potential shifts presented in Fig. 2 is not related to photovoltage effects. This conclusion is not limited to iron oxides, since in Fig. 3 a similar effect is observed with a Zn foil covered by a macroscopic ZnO layer. Again, immediate and completely reversible laser-induced potential changes are detected and the energy level of the large ZnO bandgap ($E_g > 3$ eV) is not exceeded by the 785 nm laser.[8]

A contrasting case is shown in Fig. 4 for a highly reflective Si substrate. When a 785 nm beam of 100 mW is focused on a Si wafer below a KP needle, an instantaneous, large potential increase is observed, which slowly relaxes toward the initial value after the laser is turned off. The polarity of potential change is opposite, but the general shape is similar to the transients shown in Figs. 1 to 3, and to those that resulted when focusing a CW 532 nm beam on hematite at high RH.[1] However, in this case, the signal corresponding to the substrate/tip separation distance changes when the light is turned on and off, as shown in Fig. 4. It indicates that the laser beam reflected off of the mirror-like wafer surface and irradiated the KP needle, which changed the electrical and capacitive properties of the KP needle. Under these conditions, meaningful Volta potential measurements are not possible. The transients shown in Fig. 4 are influenced by parasitic signals in the electrical circuit of the KP and therefore hardly reflect sample properties. In particular, the polarity of the potential change and the slow relaxation of the potential upon turning off the laser probably result from artifacts associated with the circuitry rather than physical properties of the sample. Very reflective surfaces should be consequently analyzed by separate spectroscopic and electrochemical measurements at the same sample spot and not by a simultaneous KP-Raman spectroscopy experiment. The data presented in Fig. 4 also imply that artifacts from reflected laser light might influence the characteristics of photovoltage transients recorded with a KP on inorganic thin layers like ZnO deposited on carriers such as Si wafers or solar cell devices.[3–5]

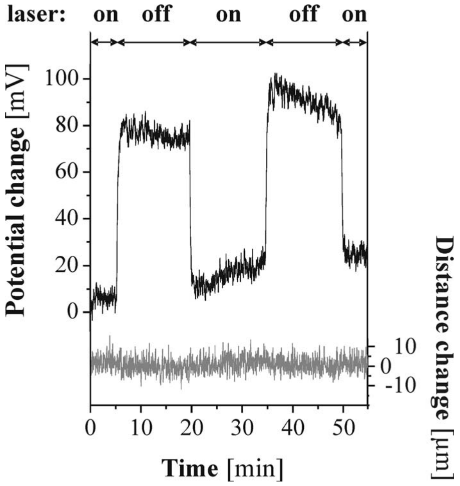

Figure 3. Potential and distance transients recorded on a ZnO-covered zinc foil irradiated with a 785 nm laser beam (output energy: 100 mW) focused beneath the KP needle.

Conclusions

In contrast to potential transients obtained with a 532 nm laser, measurements performed at a longer wavelength (785 nm) induce reversible reduction and instantaneous adjustment of Volta potentials

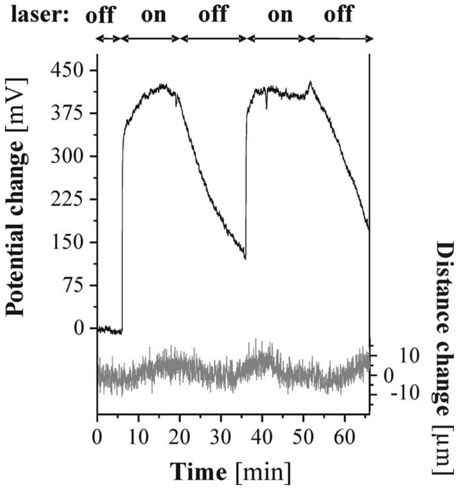

Figure 4. Potential and distance transients recorded on a Si wafer irradiated with a 785 nm laser beam (output energy: 100 mW) focused beneath the KP needle.

on steel, hematite-covered steel and ZnO-covered Zn. Complete and instantaneous recovery of the Volta potential was observed under all conditions for these electrodes when 785 nm light was used. Photovoltage effects are unlikely to contribute to the results. Light-induced potential shifts do not linearly increase with increasing laser power. In contrast, reflections of the laser beam off of reflective Si wafers raise the potential, suggesting that KP and Raman spectroscopy measurements should not be simultaneously performed on mirror-like surfaces. Undesired irreversible laser-induced potential shifts can be consequently avoided employing low energetic lasers and minimized power output on matte finished sample surfaces, which confirms a general applicability of KPs for electro-optical analysis.

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