

Potential role of hole accumulation via photoionization and electron tunneling during laser-assisted field evaporation of insulators with high energy photons

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The laser-assisted field evaporation of oxides by deep UV (257.5 nm wavelength, 4.8 eV photon energy) and UV (355 nm, 3.5 eV) laser light was investigated by measuring the detection rate as a function of laser pulse energy. The experimental approach, where the voltage and hence the electrostatic field are held constant, was performed on the metallic alloy Ni-20Cr as well as chromia and SrTiO₃. The detection rate was recorded as a function of laser pulse energy as well as field estimates. The experiments confirm evaporation being facilitated by a thermal pulse via the laser for the metallic alloy, thereby validating the strategy. For oxides, the relation did not follow an Arrhenius law expected for a temperature pulse. Instead, the measurements closely followed an expression of the form $Ax_1 + Bx_2^2 \exp\{-\frac{C}{x_2}\}$, where $x_1 = E_{\text{Laser}}$ and $x_2 = (T_0 + k E_{\text{Laser}})$ with A , B , C , and k being constants, T_0 the base temperature, and E_{Laser} the laser pulse energy. Hence, we propose that the evaporation mechanism involves a reduction of the energy barrier through accumulation of charge carrier holes at the apex. Hole generation occurs via photoionization and photoinduced tunneling of electrons. Investigations with a variation of the electrostatic field during evaporation of chromia underline the proposed mechanisms. Previously unexplained laser-assisted field evaporation of MgO, Fe₃O₄, and GaN in atom probe experiments with UV laser light fits with the new observations. Further theoretical and experimental research is needed to confirm or refute the proposed mechanism.

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I. INTRODUCTION

Atom probe tomography (APT) is a highly localized material analysis technique that can attain chemical information with nearly atomic spatial resolution. The method is sensitive to all elements and is based on the field evaporation of ions in a high electrostatic field. A needle-shaped specimen with an apex radius below 100 nm is exposed to high voltages, thereby reaching electrostatic fields in the range of tens of volts per nanometer. For conducting materials an additional voltage pulse ionizes the atoms and accelerates them to a position-sensitive detector, allowing it to identify the x and y position and, furthermore, the ion species by time-of-flight mass spectrometry. The temperature of the specimen is usually between 20 and 80 K. A reconstruction algorithm calculates the z position of the ions from the measurement sequence [1]. Historically, the technique was limited to conductive materials, i.e., metals and alloys [2–4]. However, lasers with short pulses that enable a high energy density in the focal spot opened the technique to nonconductive materials [5–10]. Hereby, the

voltage pulses are replaced by laser pulses, while the field is still created by the standing voltage. The widely accepted mechanism for field evaporation with laser light, for at least ultrashort (100-fs) pulses, is a thermal pulse [4,10]. The effect of optical rectification was introduced to explain nonlinear processes during ion emission, but was later found not to be dominant [11,12]. In the case of metals, the electrons absorb the energy of the photons before transferring the energy to the lattice atoms [13,14]. The voltage to maintain a constant detection rate (DR) as a function of laser pulse energy (LPE) follows a negative linear trend for metals, whereas semiconductors with a small band gap may show a saturation effect with laser intensity [15,16]. The band gap is described to decrease in the electrostatic field and can potentially even collapse, leading to a metallic behavior during field evaporation [17,18]. Conversely, in high-band-gap semiconductors, vacancy defects at the sample surface are sufficient to allow strong laser absorption, followed by lateral and axial heating [19]. After the pulse, the specimen is cooled through the shank and evaporation stops. Depending on the heat dissipation, peaks in the mass spectrum show more or less thermal tails due to delayed cooling and evaporation [20].

Equation (1) describes the evaporation rate $\Phi_{\text{evap}}(t)$ during thermally assisted field evaporation.

$$\Phi_{\text{evap}}(t) \sim \exp \left\{ -\frac{Q(t)}{k_B T(t)} \right\}. \quad (1)$$

It is dependent on the height of the energy barrier for ion desorption, which can be simplified as a function of the

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electrostatic field $F(t)$ as $Q(t) = Q_0(1 - \sqrt{\frac{F(t)}{F_0}})$. Here, $T(t)$ is the absolute temperature, k_B the Boltzmann constant, and F_0 the evaporation field of the specimen [4,21,22]. The terms are shown as being time dependent since time-of-flight mass spectroscopy is used to identify the ion species. While voltage pulses reduce the energy barrier for evaporation due to the increase in electrostatic field, laser pulses usually are understood to increase the temperature of the specimen to initiate evaporation.

The formalism in this model [Eq. (1)] is a somewhat simplified description on the global scale of the APT specimen, averaging thousands of ion desorptions. On the atomic level, things like surface steps as well as atomic rearrangements and surface reconstructions before and after ion desorption come into play [23–26]. Furthermore, the bonding characteristics as well as the energy barrier for different elements, especially for multispecies materials like oxides, influence ion evaporation [27,28].

A recent parameter study, by some of the authors of this publication, on the field evaporation of chromia with deep UV laser light showed evaporation over several orders of magnitude of LPE [29]. Even LPEs as low as 0.03 pJ resulted in smooth evaporation with only limited background. The O content saturated at low LPEs close to the expected stoichiometry, presumably due to postionization of otherwise neutral dissociation products [29]. A similar dependence of the O content on the LPE as well as wide ranges of LPE has been observed by Devaraj *et al.* for UV laser-assisted field evaporation of magnesia (MgO) [30]. APT investigations of magnetite (Fe₃O₄) with UV laser light also showed a wide range of possible LPEs [31]. Another study on the evaporation of GaN using UV laser light showed evaporation at low LPEs independent of the base temperature [32]. Chiaramonti *et al.* developed a setup for APT with extreme UV radiation via a high harmonic generation system based on noble-gas-filled capillaries [33]. Depending on the identity of the noble gas, wavelengths between 28 and 50 nm could be achieved [34]. These wavelengths correspond to photon energies of 25–45 eV. Evaporation could be achieved for different oxides and they discuss that the introduced energy of a single pulse is too low to heat the apex of the specimen significantly and propose that a direct athermal photoionization with a thermal desorption might take place [33]. All these observations on insulating materials cannot be explained by thermal pulsing and there has been no encompassing understanding of the underlying mechanism so far.

In addition to thermal evaporation, photoionization of semiconductors has been observed. Tsong [35] proposed three pathways for this process: (i) direct excitation of an electron of a surface atom to the conduction band of the material, (ii) excitation of the electron in the adatom and tunneling into the material, and (iii) generation of a hole in the valence band by excitation from the photon in the material and tunneling of the electron from the adatom. His observations indicated pathway (i) for Si as well as multiphoton excitations. Similarly, Gilbert *et al.* [36] as well as Mazumder and co-authors [37] report on photoionization from femtosecond laser pulses with low LPE in Si. Photoionization is not expected to play a role for metallic materials since there is no band gap and any

ionization should be re-neutralized by one of the abundant and highly mobile free electrons [35].

Thompson *et al.* showed two evaporation modes for Si with different resistivity [38]. One mode was apparent at test temperatures below 110 K and showed evaporation independent of the temperature and resistivity. Furthermore, 1 at. % of H was measured in the mass spectrum and seemingly hydrogen was involved in the evaporation process. The other evaporation mode was exponentially dependent on temperature. Gas-promoted field evaporation was described early on in the development of the atom probe technique, where chemisorbed gases would alter the bond between metal atoms and facilitate field evaporation [39].

Tamura *et al.* theoretically investigated the electric potentials during field evaporation of insulators with photoinduced holes [40]. In contrast to metals, the field is only partly screened at the surface and a gradient of the electric potential is present inside the material [17,40,41]. Light pulses with photon energy higher than the band gap of the material can lead to the creation of an electron-hole pair, where the electron gets excited to the conduction band and a hole in the valence band remains. The electric potential gradient separates these charge carriers. This leads to an accumulation of holes at the apex' surface and in turn to a reduction of the energy barrier for desorption [40,42]. These calculations show that $Q(t)$ in Eq. (1) may be reduced by the presence of holes at the apex. Ions would still desorb by thermal activation to overcome the energy barrier.

Electron emission in a high electrostatic field can be described by tunneling through a triangular barrier, also known as Fowler-Nordheim tunneling [43]. It is not limited to metals, but is also used to describe conduction mechanisms in semiconductor devices [44,45]. Equation (2) is the Fowler-Nordheim (FN) equation with an energy barrier Q_{FN} in an electrostatic field F :

$$j = A \frac{F^2}{Q_{FN}} \exp \left\{ -\frac{B Q_{FN}^{3/2}}{F} \right\}, \quad (2)$$

where A and B are constants that include, among other things, the mass and charge of the electron. Historically, the equation was found for electron emission from metals, with the sample at negative potential. A higher electrostatic field reduces the angle of the triangular barrier and thereby the width, and a higher flux is achieved. An energy input in terms of temperature or high energy photons can elevate electrons to an energy level higher than the barrier or to a level where the barrier is narrower and enables tunneling. Already at the time, the interplay between field, temperature, and photon illumination was recognized [43,46–48]. The dependence of electron flux on temperature is shown in Eq. (3):

$$j_T \sim T^2 \exp \left\{ -\frac{\text{const}}{T} \right\}. \quad (3)$$

Similarly to temperature, photoexcited electrons can be influenced by the field, and with a negative potential applied to a field emitter the effective work function of a material can be lowered [49]. Electron tunneling has been shown to be involved in ionization processes in field ion microscopy [50].

Above, the working principle of APT and the development of laser-assisted field evaporation was established, and several

publications where the classical understanding of the evaporation mechanism as a thermal pulse does not explain the observations were mentioned. Different alternative explanations describing possible mechanisms were introduced as well as the background for electron tunneling in an electrostatic field. Section II describes the investigated materials and the measurement parameters and procedures. Section III starts with the results on the metallic alloy, showing the expected behavior for a thermal pulse. In comparison, the experimental observations on oxides (Secs. III B–III D) are different and the contradictions to classical understanding of a thermal pulse are discussed in Sec. IV A. A possible explanation involving the reduction of the energy barrier by the accumulation of holes, where hole generation is happening by photoionization and photoinduced electron tunneling as an indirect evaporation mechanism, is presented in Sec. IV B. Furthermore, the evaporation of chromia in UV laser light (Sec. IV C), the influence of the band gap and the work function (Sec. IV D), as well as similar previous observations in literature (Sec. IV E) are discussed. Influences on the atomic level of ion desorption (surface reconstructions, bonding characteristics) should be similarly present for both of the discussed models. The paper is therefore limited to the description of evaporation phenomena on the global scale of the APT specimen.

II. MATERIALS AND METHODS

APT specimens were investigated from a metallic alloy containing about 80 wt. % Ni and 20 wt. % Cr (Ni-20Cr), thermally grown chromia (Cr_2O_3), a chromia coating prepared by chemical vapor deposition (CVD) and [100]-oriented SrTiO_3 . A two-step electropolishing process with perchloric acid solutions was performed on Ni-20Cr wire to achieve sharp specimens [51]. The chromia was grown on a Ni-base alloy and contains about 3 at. % other elements, mostly Ti. Ti is in solid solution as well as segregated to grain boundaries. In addition to this material, high purity chromia with less than 0.03 at. % of other elements was fabricated by CVD. Deposition was carried out in a commercial reactor at 950 °C and at 5.5 kPa pressure. Chromium chloride (CrCl_3), CO_2 , HCl , H_2 , N_2 , and Ar were used as reactive and carrier gases, respectively. Liftout and sample preparation were performed with the focused ion beam (FIB) of a dual-beam FEI Versa 3D workstation (Hillsboro, OR, USA) using well-known procedures [52,53]. The thermally grown chromia is the same material as in Ref. [29] and more details can be found there as well as in Ref. [54]. The APT specimens were composed of 1–3 μm of chromia at the apex and welded with Pt to the conductive Si coupon post. The SrTiO_3 sample used is commercially available and was oriented along the [100] growth axis for the APT experiment.

Most APT experiments were performed on a CAMECA LEAP 6000 XR (Madison, WI, USA) at 40 K test temperature, 200 kHz frequency, and different LPEs and DRs. The tool has 52% detection efficiency and is equipped with a deep UV laser system that provides laser pulses with 257.5 nm wavelength corresponding to 4.8 eV photon energy. The Ga-implanted top layer from FIB processing was removed in the APT in the case of the oxide samples before the actual experiment. Experiments with intermittent constant voltage were performed at

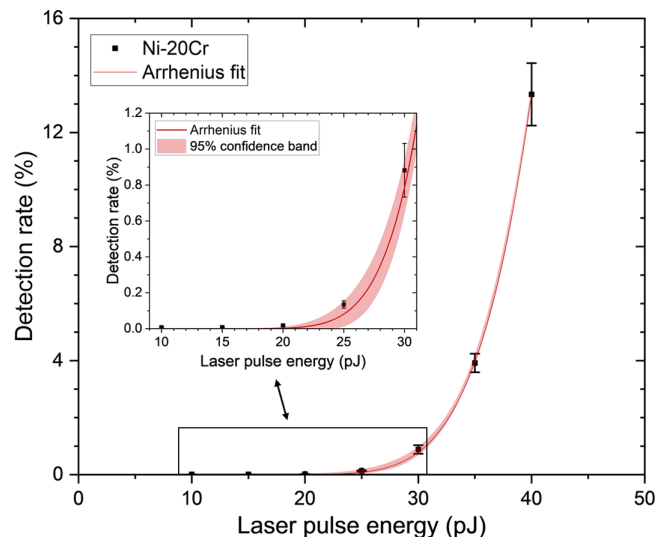


FIG. 1. DR as a function of LPE during constant-voltage experiments with deep UV laser light (257.5 nm, 4.8 eV) for the metallic alloy Ni-20Cr. The inset shows a detailed section of low LPEs. An Arrhenius fit is depicted as well.

LPEs between 1 and 70 pJ. After initial evaporation was established, the voltage was kept constant and the DR at a different LPE was recorded. To avoid the influence of tip blunting, the voltage was adjusted to match the previous DR at the initial LPE before repeating the procedure for the next LPE. More details on the measurement procedure are described in the Supplemental Material [55]. Additionally, the DR of chromia as a function of electrostatic field was investigated at different voltages from 4702 to 7160 V in steps of 200 V for experiments with 5 and 50 pJ, as well as at 40 and 80 K test temperatures, respectively. The correlation of DR with field for Ni-20Cr was investigated at 40 K with 30 pJ LPE between 4200 and 5400 V as well as with target DRs between 0.25 and 8%. The field at the metallic sample was estimated via charge state ratios (CSRs) of $\text{Ni}^{++}/\text{Ni}^{+}$ according to Kingham *et al.* [56,57]. The same chromia APT specimens were investigated on a CAMECA LEAP 5000 XR, equipped with a UV laser (355 nm, 3.5 eV), with LPEs between 5 and 220 pJ. The field variation of chromia in UV laser light was performed at 50 and 200 pJ between 4600 and 6500 V. Measurement data were exported from the commercial software AP Suite 6.3 and processed and visualized in OriginPro 2023.

III. EXPERIMENTAL RESULTS

A. Constant-voltage experiment on metallic alloy Ni-20Cr

Figure 1 shows the DR as a function of LPE while the voltage is held intermittently constant for the metallic alloy Ni-20Cr. The specimen shape and its blunting led to an increase in standing voltage from about 3450 to 3545 V, or 2.8%, during the collection of little more than 10^6 ions. The DR decreased slightly at high LPEs during the holding segments at constant voltage due to specimen blunting. Therefore, only the initial 100 000 ions were selected for averaging in the case of 35 and 40 pJ. The DR, sample windows, LPE, and voltage as a function of ion sequence number during

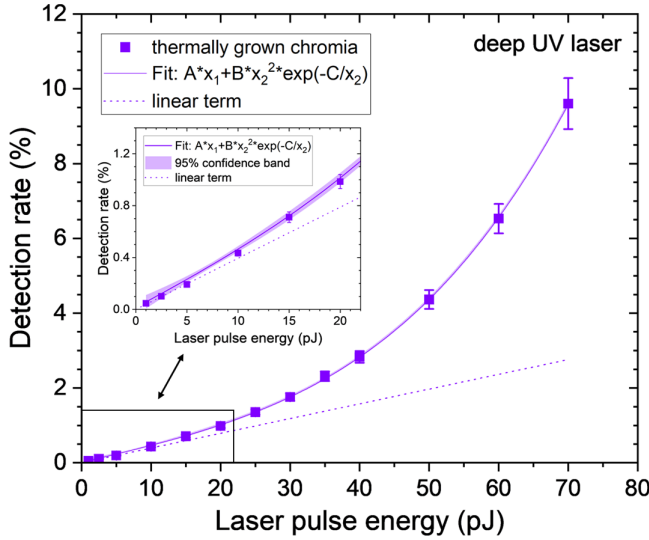


FIG. 2. DR as a function of LPE for thermally grown chromia during constant-voltage experiments with deep UV laser light (257.5 nm, 4.8 eV). The solid line shows the apparent fit function with 95% confidence range and the dashed line shows the linear term of the fit. The inset provides a detailed depiction of low LPEs.

the experiment can be found in the Supplemental Material in Fig. S1 [55].

The peak temperature during laser pulses has been investigated by experiments as well as numerical studies [12,15,16,58]. The emerging CSRs during experiments were indicative of the temperature at the time of the pulse, providing an indirect measure. Both approaches indicate that the peak temperature during the pulse for metals is proportional to the LPE [15,16]. Thus, T can be substituted with LPE in Eq. (1). The observed Arrhenius fit, corresponding to the expected behavior from thermal pulsing, validates the experimental approach for the investigation of evaporation mechanisms.

B. Constant-voltage experiments on oxides

Figure 2 shows the DR as a function of LPE at constant voltage for the thermally grown chromia specimen. The chromia specimen exhibits a small shank angle and hence shows minimal change in voltage of about 15 V during the entire experiment with about 10^6 collected ions (see Fig. S2 in the Supplemental Material [55] as well as the discussion in Ref. [29]). At low LPEs the DR depicts a nearly linear relationship with LPE. At higher LPEs, the data points significantly deviate from a linear fit. The evaporation does not simply match the assumption of an additional thermal contribution, as will be discussed in Sec. IV A. However, the whole range of data points can be fitted with Eq. (4), where $x_1 = E_{\text{Laser}}$ and $x_2 = (T_0 + k E_{\text{Laser}})$:

$$A x_1 + B x_2^2 \exp\left\{-\frac{C}{x_2}\right\} \quad (4)$$

A , B , C , and k are constants, and E_{Laser} is the LPE. The fit is depicted with the 95% confidence range in Fig. 2.

The influence of base temperature during deep UV laser-assisted field evaporation of chromia was investigated during

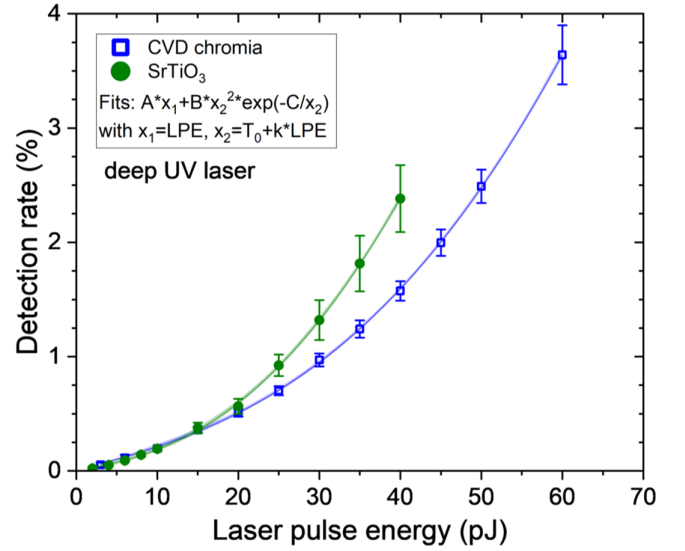


FIG. 3. DR as a function of LPE for CVD chromia and SrTiO_3 during constant-voltage experiments with deep UV laser light (257.5 nm, 4.8 eV). The solid lines show the same fit function as for thermally grown chromia (see Fig. 2) with 95% confidence range (barely visible as the range is very small).

a parameter study and showed limited impact on the measurements [29]. LPE variation experiments at constant voltages of 5600 and 5800 V at 40 and 80 K were performed on the same specimen of chromia (see Fig. S3 in the Supplemental Material [55]). Data of all four experiments conform to the same shape as in Fig. 2, showing a limited influence of base temperature in comparison to the electrostatic field of each measurement point.

Figure 3 shows further results with the presented methodology of intermittent constant-voltage experiments with deep UV laser pulses. The observed correlation of DR as a function of LPE for CVD chromia and SrTiO_3 fits well with Eq. (4), just as for thermally grown chromia. The CVD process allowed for a high purity material with less than 0.03 at. % concentration of other elements. The correlation is consistently observed for several measurements on different APT specimens from the prepared liftouts. Furthermore, the observation of the same correlation on SrTiO_3 shows that the underlying evaporation mechanisms might be more widely applicable.

C. Dependence of evaporation rate on electrostatic field

Figure 4 depicts the DR as a function of electrostatic field for thermally grown chromia as well as Ni-20Cr during deep UV laser-assisted field evaporation. The CSR of $\text{Cr}^{++}/\text{Cr}^+$ ions during evaporation of chromia shows a consistent trend as a function of LPE (shown in Fig. S4 in the Supplemental Material [55]) and hence can be used to compare the field strength between experiments. Data points from an initial target DR of 0.5% were used to put the experiments into relation with each other and all further data points are derived from the voltage steps. This means that the relative field estimate is accurate. See the Supplemental Material for the depiction of field estimate as a function of CSR [55]. Figure 4 shows four curves for thermally grown chromia corresponding to

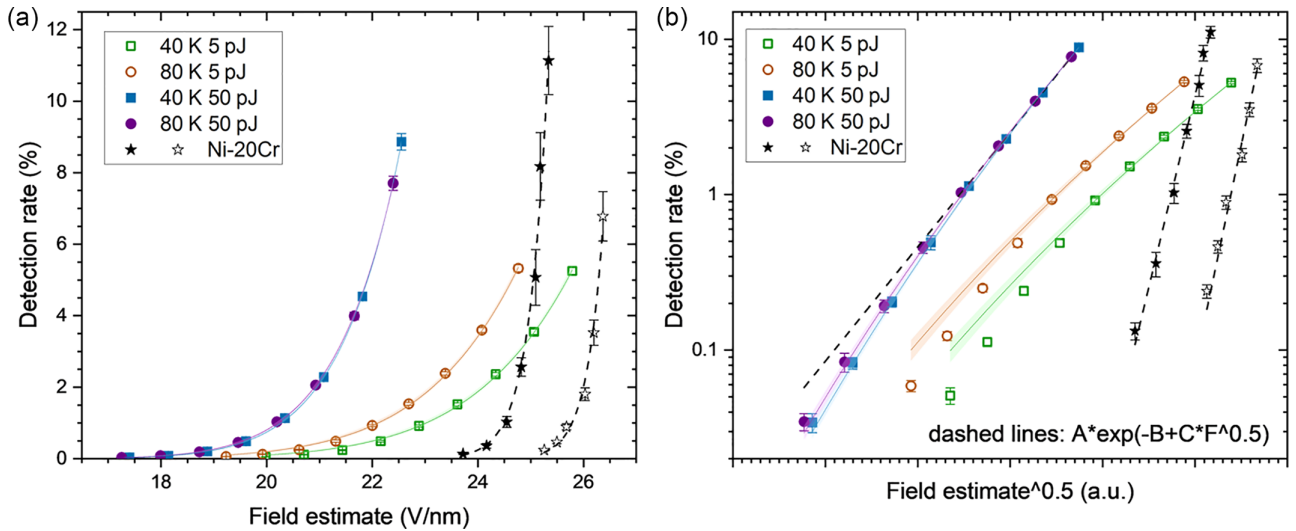


FIG. 4. DR as a function of field estimate for thermally grown chromia as well as Ni-20Cr in deep UV (257.7 nm, 4.8 eV) laser-assisted field evaporation. The solid lines show the fit functions for Eq. (2) with 95% confidence range. The dashed lines represent a fit for classical thermal pulsing. For further details see the text.

four experiments with 5 and 50 pJ LPE at 40 and 80 K test temperature, respectively. The parameters were chosen to show, on one hand, experiments with low LPE, where no significant temperature increase is expected (5 pJ LPE), and, on the other hand, a high LPE, where one would expect a thermal contribution due to the laser pulse (50 pJ). These experiments were conducted on the same APT specimen to ensure comparability. For the low LPE the initial test (base) temperature has a significant influence. The curves with 5 pJ are shifted relative to each other and at the same field estimate the experiment at 80 K shows more evaporation. The data points for 50 pJ are shifted toward lower fields as expected. Furthermore, they exhibit a greatly reduced dependence on initial temperature compared to the curves with 5 pJ LPE. This is consistent with a thermally enhanced process.

Experiments on Ni-20Cr are depicted in Fig. 4 as well. One experiment was conducted with different voltage steps (solid symbols) and another experiment with different target DRs (open symbols). The curves for the metallic alloy can be fitted with the expression $A \exp(-B + C \sqrt{F})$, consistent with the understanding that evaporation is triggered by a temperature increase or thermal pulsing. This correlation is a straight line when plotting logarithmic DR as a function of the square root of field estimate as visualized in Fig. 4(b). The chromia experiments do not follow a straight line. However, the experiments at high LPE match Eq. (2). The experiments at low LPE are expected to have a higher proportion of photoionization but still match Eq. (2) well. In contrast, they cannot be fitted to the expression for the classical explanation of a thermal pulse.

D. Laser-assisted field evaporation of chromia with UV laser pulses

Figure 5 shows the LPE variation at intermittent constant voltage for chromia specimens evaporated using UV laser light (LEAP 5000 XR). The curves depict a similar correlation of DR with LPE as seen in Fig. 2. The LPEs are higher than in deep UV laser light, which is in part due to the size difference of the focal spot between the instruments [59]. Thermally

grown chromia and CVD chromia show close agreement for the linear correlation of DR with LPE at low LPEs. The nonlinear part is shifted to higher LPEs for thermally grown chromia compared to CVD chromia. Fit functions according to Eq. (4) with $x_1 = x_2 = E_{\text{Laser}}$ produce reasonable fits. However, after fixing the linear coefficient, the remainder of the curve can be fitted with an Arrhenius plot similarly well. Hence, it is not possible from the data in Fig. 5(a) alone to distinguish between the underlying mechanisms, as will be discussed in Sec. IV C.

Field variations during UV laser-assisted field evaporation have been performed on thermally grown chromia with 50 and 200 pJ LPE at 40 K test temperature and are depicted in Figs. 5(c) and 5(d). Relative field changes are displayed since CSRs showed a peculiar nonmonotonic dependence on LPE (see Fig. S6 in the Supplemental Material [55]). Similar behavior was previously observed during UV laser-assisted field evaporation of Fe_3O_4 [31]. The data depicted a point where $\text{Cr}^{++}/\text{Cr}^+$ CSRs were about 25 for both experiments and further data points are calculated from the relative voltage increments. The fit with Eq. (2) shows better agreement than fits with the classical explanation of thermal pulses [dashed lines in Fig. 5(d)] similar to the experiments with deep UV laser light.

IV. DISCUSSION

A. Consideration of a thermal pulse

The comparison of constant-voltage experiments to the evaporation mechanism works under the premise that the peak temperature is proportional to the LPE. This has been investigated by experiments as well as numerical studies, and both approaches indicate that the peak temperature during the pulse is proportional to the LPE, at least for metals [12,15,16,58]. Hence, temperature can be substituted with LPE in the experiment on the metallic alloy Ni-20Cr. This shows a strong correlation with the expected Arrhenius behavior, i.e., evaporation of ions after a thermal pulse

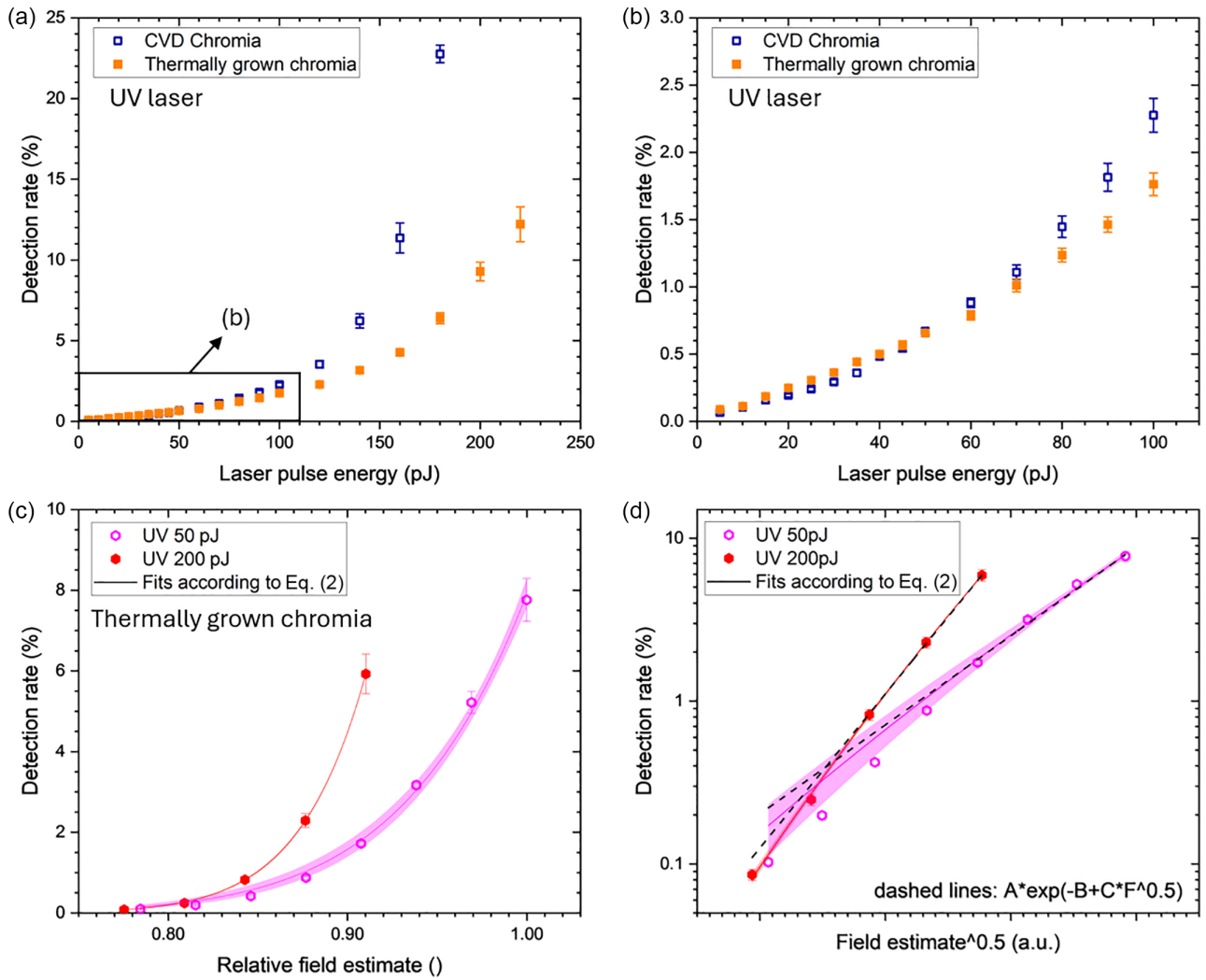


FIG. 5. (a) DR as a function of LPE in constant-voltage experiments for chromia with UV laser light (355 nm, 3.5 eV). (b) Correlation at lower LPEs, indicated by the rectangle in (a). [(c) and (d)] DR as a function of field estimate for thermally grown chromia at different LPE with fit functions according to Eq. (2) and their 95% confidence range; Dashed lines in (d) indicate the correlation for classical thermal pulsing.

due to heating from the laser, validating the experimental approach.

The interpretation of the temperature increase ΔT during laser pulses on insulators might not be as straightforward. However, the peak temperature of the semiconductor CdTe was indirectly determined similar to Ref. [58] and showed a linear correlation [32]. A numerical study by Silaeva *et al.* found that, after a linear regime for low LPEs, the proportionality changes due to a saturation of charge carriers at high LPEs [16]. Using the assumption of a linear correlation of temperature with LPE in a first attempt leads to contradictions with the classical explanation of evaporation due to thermal pulsing. In contrast to metals, where typically LPEs in the range 10–100 pJ are used, insulators have been field evaporated with fractions of pJ LPE with UV and deep UV laser pulses [29–31]. The same chromia samples as in this study have been evaporated with LPEs as low as 0.03 pJ [29]. In this range of LPEs the expected ΔT is too low to ensure timed evaporation.

The evaporation of the investigated oxides by deep UV laser pulses (Figs. 2 and 3) shows a proportional increase

of evaporation rate at low LPEs, which contradicts a simple Arrhenius fit of the data. However, this linear regime suggests that the evaporation mechanism involves direct photoionization since the DR is proportional to the LPE, i.e., to the number of photons illuminating the specimen. Another attempt to explain the observations might be to assume the superposition of photoionization as a linear contribution and a thermal pulse for the nonlinear part. Again, on one hand, a too-low ΔT would lead to DC evaporation and a high background, which is not observed. On the other hand, the assumption of a higher ΔT goes hand in hand with the assumption of a higher activation energy $Q(t)$ needed for evaporation. This contradicts the observations as well, as the oxide evaporates at lower field than the metal. This is observed in (constant-DR) runs going from the metal into the oxide, where the standing voltage decreases within the oxide part (see Fig. S5 in the Supplemental Material [55]).

Matching the observation of DR as a function of LPE to the classical explanation of a thermal pulse would require a complex dependence of ΔT as a function of LPE for non-metals, which is not available with the current understanding

of laser-matter interaction. Moreover, several other observations are different from the expectation from classical thermal pulsing:

(i) Each curve during the investigation of DR at different electrostatic field represents an experiment where the base temperature and LPE were the same while the voltage was changed. This means that the peak temperature should remain unchanged as well. As can be seen in Fig. 4(b), the expected linear relationship between the logarithmic DR $\ln(\phi_{\text{DR}})$ and $\sqrt{F}$ for thermal pulsing is only observed for the metallic alloy Ni-20Cr.

(ii) During field evaporation of metals, where the evaporation is triggered by a thermal pulse, the standing voltage decreases proportionally with the LPE [16]. During deep UV laser-assisted field evaporation of chromia the voltage and electrostatic field are correlated with the LPE as $F \sim 1 - \ln(E_{\text{Laser}})$ (see Fig. S4 in the Supplemental Material [55] as well as Ref. [29]). If a thermal pulse were the underlying cause for evaporation of chromia and SrTiO₃, one would expect observations similar to those seen in metals.

B. Thermal desorption after hole accumulation

Insulators do not screen the electrostatic field in the same manner as metals, and an electric potential gradient is present within the material for nonconductive samples [17,40,41]. This gradient causes mobile charge carriers to move depending on their sign. Due to the high voltage, electrons are attracted toward the sample stage, whereas holes, i.e., quasiparticles representing the lack of electrons, are attracted toward the apex of the APT needle. Laser irradiation above the band gap can cause the creation of an electron-hole pair followed by the separation of the charge carriers by the electric potential gradient. Tamura *et al.* have calculated the energy barrier for ion desorption from an MgO APT needle apex with different numbers of holes in the vicinity [40]. Their *ab initio* calculations show that a higher number of holes leads to a reduction in the height of the energy barrier $Q(t)$. This is intuitive since charge carriers with the same sign repel each other. An ion would then desorb by thermal vibrations, as is the current understanding of field evaporation. Taking inspiration from Tamura *et al.*'s work, we can explore the logical consequences of a potential reduction of the energy barrier. This would create the following situation: in the case of ion desorption, the energy barrier increases since the number of holes is reduced by one. Only when another hole arrives in the vicinity is the energy barrier reduced to the same level as before. In other words, a dynamic equilibrium of generation of holes and desorption of ions should establish itself.

The electric field gradient within the insulating material in combination with high photon energy laser irradiation allows for a situation where electrons may tunnel after photoexcitation. The travel direction for the electrons is in accordance with the electric potential gradient from the apex of the needle toward the stage. Tunneling can be enhanced by temperature as described by Eq. (3) and a sufficiently large number of photons may still cause a thermal pulse in the specimen. A linear correlation between the temperature and the LPE was described for insulators similar to metals [16,32]. Keeping the assumption of photoionization for the linear term and

substituting T with $(T_0 + k E_{\text{Laser}})$ in Eq. (3), the evaporation data in Fig. 2 match the expression of Eq. (4). Using the parameters of the fit, we get a temperature rise of 46 K during pulsing with 70 pJ LPE for thermally grown chromia. This moderate temperature increase should lie within the initial slope of ΔT in Ref. [16]. Hence, the assumption of a proportional temperature rise with LPE appears to be valid.

In addition to the evaporation data in Fig. 2, we can look at the variation of the electrostatic field (Fig. 4). Each experiment was conducted at a certain base temperature and with a specific LPE. Hence, each experiment should have experienced the same peak temperature. The evaporation rate as a function of electrostatic field for experiments with 50 pJ LPE shows a sound match with Eq. (2), i.e., electron tunneling through a triangular barrier. The experiments at 5 pJ LPE and high field conditions match Eq. (2) similarly well. Evaporation under low field conditions with low LPE shows a deviation that may be explained by a high portion of photoionization during the experiment. At higher fields and/or temperature the portion of photoinduced electron tunneling would be larger. In contrast to chromia, the evaporation data as a function of electrostatic field for the metallic samples show the expected match with thermal pulsing, illustrated as straight lines in Fig. 4(b).

The small temperature increase, as calculated from the fit parameters, might be the reason for the consistent trend of CSRs with different LPEs during field evaporation of chromia with deep UV laser pulses. Lower field estimates for chromia compared to the metallic Ni-20Cr alloy are consistent with observations during measurements across the oxide/metal interface (see Fig. S5 in the Supplemental Material [55]).

The evaporation phenomenon that we describe depends on the accumulation of holes at the apex of the sample. This implies that only a limited number of mobile electrons, which could neutralize the holes, should be present in the material. Furthermore, the standing voltage in combination with the evaporation of ions may lead to an internal current within the specimen [60,61]. This would increase the screening of the electrostatic field and limit the generation and accumulation of holes. Further experiments with semiconductors with different charge carrier entity and density are desired to better understand the prerequisites for hole accumulation via photoinduced electron tunneling as an indirect evaporation mechanism.

C. Discussion of UV laser-assisted field evaporation of chromia

The standing voltage during UV laser-assisted APT of chromia shows a logarithmic dependence at low LPEs and a linear dependence of the standing voltage with LPE at higher LPEs (Figs. S6 and S7 in the Supplemental Material [55]). The measured O content of chromia is dependent on the electrostatic field. Figure S6 [55] shows that field evaporation with UV laser pulses between 20 and 300 pJ LPE results in O concentrations between 50 and 58 at. %. Previous field evaporation of thermally grown chromia with UV laser illumination (20 to 115 pJ LPEs) in literature showed the O concentration to be close to the expected stoichiometry of 60 at. % as well [62]. In contrast, deep-UV laser pulses enabled evaporation over more than three orders of magnitude of LPEs between

0.03 and 90 pJ. The O concentration was strongly dependent on the electrostatic field, presumably due to postionization of otherwise neutral O from molecular dissociations [29,63]. Furthermore, a measurement across a metal/oxide interface with deep UV laser light showed a decrease in the standing voltage (Fig. S5 in the Supplemental Material [55]). All this confirms a higher evaporation field during UV laser-assisted field evaporation compared to deep UV laser light. It seems possible that during UV laser-assisted APT of chromia, photoinduced electron tunneling is dominant during high field conditions at low LPE. Conversely, classical thermal pulsing might be dominant at high LPEs where a high thermal energy input is expected. Note that both phenomena can be in effect simultaneously.

The graphs in Fig. 5(a) depict a shift of the nonlinear part of the curves between thermally grown chromia and CVD chromia. A general trend cannot be deduced from this as only one specimen was recorded for each material. While differences between specimens might play a role, it is worthwhile to consider that more defects in the thermally grown chromia should in principle allow more absorption of the laser energy leading to a larger temperature increase. This would shift the curve in the opposite direction than the observed difference between thermally grown and CVD chromia. However, possible recombinations of holes with surplus electrons from impurities would render the evaporation less effective and cause a shift in the observed direction.

As discussed in the Introduction, temperature, field, and photon energy affect the probability of electron tunneling. In the case of UV laser light, more energy has to come from either a higher temperature of the sample or a higher field, leading to the narrowing of the energy barrier. In contrast to deep UV laser pulses, the CSRs during field evaporation with UV laser light showed a peculiar dependence on the LPE for chromia (see Fig. S6 [55]) as well as Fe_3O_4 [31]. The reason for this might be the transition from the hole-limited evaporation phenomenon to evaporation mainly caused by a thermal pulse. Large thermal tails are observed for high LPEs during UV experiments (see Fig. S8 in the Supplemental Material [55] as well as Ref. [62]). In contrast, the absence of significant thermal tails in deep UV experiments suggests only a limited temperature increase. A marginal thermal tail is visible several orders of magnitude below the peak maximum [29]. The presence of thermal tails does not necessarily distinguish between classical thermal pulsing and photoinduced electron tunneling since tunneling is also thermally enhanced and delayed desorption is possible.

D. Discussion on band gap and work function

The photon energy of the deep UV experiments presented here (257.5 nm wavelength, 4.8 eV photon energy) is higher than the band gap of 2.9–3.55 eV of chromia [64,65]. Thus, photoionization should in principle be possible. UV laser pulses (355 nm wavelength, 3.5 eV photon energy) have similar photon energy as the band gap. It has been reported that the high electrostatic field at the apex of the APT sample leads to a compression of the energy bands [17]. Therefore, the UV laser pulses with 3.5 eV photon energy should overcome the band gap of the material as well. Tsong [35] proposed direct

photoionization for photon energies above the band gap of the material. Our experiments on chromia indicate that both UV and deep UV exhibit photoionization as observed by the approximately linear part of the curves in Figs. 2 and 5. It stands to reason that the accumulation of holes at the apex of the specimen is a prerequisite for the photoionization observed here. As discussed above, the desorption of an ion raises the energy barrier for the next ion until another hole within the material moves into the proximity. Ion desorption is therefore rate limited by the generation of new holes. Photon energies above the band gap can elevate an electron into the conduction band and the presence of a potential gradient within the insulator material allows for the removal of the electron from its former position, leaving a hole behind. Photoinduced electron tunneling can happen in parallel and is dependent on the tunneling probability of the electrons, thus depending on photon energy, temperature, and electrostatic field. SrTiO_3 has a band gap of 3.25 eV [66,67] and hence should evaporate by this mechanism for both lasers. The limited yield during experiments with UV laser light might be due to mechanical failure in the high electrostatic field.

Chromia has a work function of about 4.5 eV [68,69] and SrTiO_3 has a work function of 4.3 eV for TiO_2 terminated surfaces [70]. Since the photon energy of the deep UV laser used here (4.8 eV photon energy) is higher than the work functions, a photon has high enough energy to cause the removal of an electron from its atom due to the photoelectric effect alone. In contrast, laser-assisted evaporation of chromia in UV light (3.5 eV photon energy) does not provide enough energy to the electrons for direct removal. A recombination of the electron and its corresponding hole right after creation might happen for UV laser light. In the case of deep UV laser light, the electron is spatially removed from the hole. The photoelectrons leave the material and consequently cannot contribute to sample heating at the apex of the APT needle. This can explain the limited thermal pulse despite a higher expected absorption of chromia in deep UV laser light.

Arnoldi *et al.* report on the influence of resistivity, LPE, and charge carrier density during field evaporation with UV laser light in a straight-flight-path instrument [60]. A high number of charge carriers would reduce the resistivity significantly and potentially turn a weak insulator conductive. In their work, a voltage drop at the apex is only observed for the highly resistive materials MgO and SiO_2 . Following their calculations, we would expect diminishing electrostatic field within the chromia APT specimens due to the high number of charge carriers. However, since the deep UV laser light has higher energy than the work function of the material, we can expect the generated photoelectrons to be missing from the internal current. Furthermore, field evaporation is happening at lower standing voltages in deep UV laser light than previously expected from UV experiments (see Fig. S5 [55]). Hence, the electric field is not so readily screened within the specimen even for materials with lower resistivity. We see a phenomenological difference between the time-of-flight spectra of chromia during constant DR experiments with UV and deep UV laser pulses, as illustrated in Fig. S9 in the Supplemental Material [55]. Note that our data were recorded on instruments equipped with reflectrons for energy compensation. Investigations with straight-flight-path

instruments are highly desired to compare to the experiments in Ref. [60].

The application of laser pulses with photon energies larger than the work function may increase the efficiency of hole generation between the instruments manifold and more theoretical investigations are needed as well as experimental work to explain the behavior.

E. Comparison to other previously unexplained field evaporation of insulators

Deep UV laser-assisted field evaporation of chromia showed strong dependence on electrostatic field [29]. A similar dependence of the O content on the LPE, over a similarly wide range of LPEs, has been observed by Devaraj *et al.* for UV laser-assisted field evaporation of magnesia (MgO) [30]. The authors furthermore showed that the electric field, indicated by the CSR $\text{Mg}^{++}/\text{Mg}^+$, is correlated with LPE and O content in a similar manner to chromia. Magnesia has a high band gap (7.7 eV) and the reported work functions are 4.2–5.1 eV [71]. However, in addition to sub-band-gap states [72], the relevance of the lifetime of holes at corner sites in conjunction with photoexcitation was discussed [30,73]. The experimentally observed ion flux as a function of LPE and applied voltage in Ref. [42] fits well with Eq. (2), suggesting that the same mechanism is at play for magnesia as for chromia. Similarly, APT investigations of magnetite (Fe_3O_4) with UV laser light also showed a wide range of possible LPEs [31]. Another study on the evaporation of GaN (3.4 eV band gap [74], approximately 4 eV work function [75]) using UV laser light showed evaporation at low LPEs independent of the base temperature [32]. In these studies, as well as for chromia in deep UV laser light, the voltage and electrostatic field are correlated with the LPE as $F \sim 1 - \ln(E_{\text{Laser}})$. This supports the assumption that the same mechanisms were in effect. Further previously unexplained observations during laser-assisted field evaporation of insulators (and semiconductors) might be understood in the near future [76].

V. CONCLUSION

In this work, the evaporation of oxides by deep UV and UV laser-assisted field evaporation was investigated by measuring the detection rate (DR) as a function of laser pulse energy (LPE). Experiments with intermittent constant voltage, and hence constant field, were performed on the metallic alloy Ni-20Cr as well as differently manufactured chromia and SrTiO_3 . The experiments confirm the classical understanding of evaporation triggered by a thermal pulse induced by the laser for the metallic alloy. In contrast, the measurements on the oxides closely followed an expression of the form $Ax_1 +$

$Bx_2^2 \exp\{-\frac{C}{x_2}\}$, where $x_1 = E_{\text{Laser}}$, $x_2 = (T_0 + k E_{\text{Laser}})$, and E_{Laser} represents the LPE. It is proposed that the evaporation mechanism involves a reduction in the energy barrier via hole accumulation at the apex, where the flux of evaporating ions should be limited by the generation of new holes. DR as a function of LPE for the oxides shows an approximately linear regime corresponding to photoionization for low LPEs. The non linear part at higher LPEs as well as the DR as a function of electrostatic field follow the same expressions as electron tunneling flux. Hence, the DR seems to be rate-limited as described by a superposition of photoionization and photoinduced field tunneling of electrons. Intermittent constant-voltage experiments of chromia with UV laser light show similar correlation of DR as a function of LPE with a linear regime at low LPEs. The nonlinear part might represent an edge case between photoinduced electron tunneling in high field conditions and classical thermal pulsing at high LPEs. Discerning parameters of the materials, such as band gap and work function, are discussed. The lack of (negative) charge carriers might be the critical prerequisite for the proposed mechanism and a photon energy larger than the work function may increase effectiveness significantly. Previously unexplained evaporation of MgO, Fe_3O_4 , and GaN in UV laser-assisted field evaporation show the same dependence of the electrostatic field on LPE as chromia, suggesting that the same processes are at play. Further theoretical and experimental research is needed to confirm or refute the proposed mechanism.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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