Femtosecond Laser Textured Surfaces for Radiative Cooling: Black Metals

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Article

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Abstract: There is a growing need for cost-effective methods for modifying the surfaces of a wide range of materials over large areas. Here, low reflectance $R < 2\%$ surfaces have been created over the near-to-mid IR spectral window of $2 - 20$ μm by ablating W, Al, and Cu with high average intensity 20-120 TW/cm^2 200 fs laser pulses at 1030 nm wavelength. The resulting chemical modification of the surfaces after laser ablation at ambient room conditions was assessed with X-ray photoelectron spectroscopy (XPS). The results show a consistent decrease in the metallic component together with an increase in metal oxides. Energy dispersive spectroscopy (EDS) showed a similar increase in oxygen content over a micrometer depth scale. The reduced refractive index of the metal oxides compared to the corresponding metals contributes to the reduction in infrared (IR) reflectance, together with the 3D hierarchically textured surface structure. IR-black metals show great potential for radiative cooling at elevated temperatures relevant to industrial and space applications.

Keywords: femtosecond laser ablation; high-intensity; direct energy deposition; radiative cooling; anti-reflective surfaces

1. Introduction

The black appearance of a surface in the visible spectral range can be caused by spectrally broadband absorption or by the anti-reflective nature of the surface [1,2]. Diminishing reflectivity $R \to 0$ in the absence of transmittance $T \to 0$ (a thick sample) corresponds to the high absorbance $A \to 1$, in accordance with energy conservation $A + R + T = 1$ (here scattering is accounted by reflection and absorption). Such anti-reflective black surfaces have a great potential for perfect emitter or radiative cooling applications. Radiative cooling relies on high reflectance of solar irradiation (primarily in the short-wave range of $0.15 - 2.5$ μm) and high emissivity in the mid-IR range ($3 - 25$ μm). Optical coatings, such as metals and metal oxide layers, have been demonstrated to have significant potential

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in this area by forming anti-reflective coatings (high emittance) in the atmospheric transparent window ($8-13$ μm) [3]. These coatings effectively reflect short-wave solar radiation while emitting mid-IR radiation through the atmospheric window to the outer space, thereby cooling the surfaces without energy consumption. However, such emitters or anti-reflective metasurfaces require precise and complex fabrication processes with control of layer thickness, periodicity and material composition [4]. This usually involves advanced high-vacuum manufacturing techniques [5].

Laser ablation with ultra-short <0.5 ps pulses at high-intensity $0.1-1$ PW/cm^2 opens new pathways for material processing by direct energy and momentum deposition. High-temperature and high-pressure phases, as well as new composite materials, can be created due to ultra-fast thermal quenching.

1.1. Direct Laser Writing (DLW): A Synthesis Tool for New Materials

Ultra-short sub-1 ps ($<10^{-12}$ s) pulses focused into a focal spot with a diameter comparable with the wavelength $d\sim\lambda\approx 1$ μm can create extreme pressures inside transparent materials within the focal volume, which undergo highly localized ionization into the plasma state [6]. The typical pulse intensity is in the $10^{13}-10^{14}$ W/cm^2 window, while the light-induced damage threshold is $\sim 10^{13}$ W/cm^2 $=10$ TW/cm^2. The dielectric breakdown is driven by highly nonlinear absorption due to multi-photon, avalanche, and tunneling processes, which leads to energy deposition inside the skin depth of tens-of-nm of absorptive plasma (converted from a solid-state dielectric). The energy deposited into a small volume creates a high pressure by definition: J/m^3 $\equiv$N/m^2, i.e. Pa in SI units. Pressures up to 1 TPa (10 Megabar) could be created and were consistent with a nano-void (empty volume) formation inside crystalline sapphire [6]. This method was used to create high-pressure phase Si nanocrystallites by focusing fs-laser pulses at the interface of Si and a thermally grown oxide [7]. The same Si phases were also found in a Si wafer irradiated at ultra-relativistic intensity 7.4×10^{22} W/cm^2 pulses of 30 fs duration [8]. The generation of energetic MeV-electrons contributed to the strong back-side ablation of ~ 0.5 mm wafer, structural modifications, and formation of new high-pressure phase nanomaterials at the edge of ablation crater [8], by using a direct laser writing approach. This synthesis method can be used to produce patterns of 2 - 20 nm nanoparticles of new phases inside the volume or on the surface of the host material. For binary compounds, e.g., GaAs, decomposition and phase separation are compounding factors in the quest to control phase formation and hyper-doping [9]. Alloying very different materials at the interface, e.g., Si and Cr using fs-laser irradiation, is feasible [10] (Supplement in ref. [10,11]). Interestingly, W metal and borosilicate glass have comparable thermal expansion coefficients, making their welding practical.

Nanostructures can be used to produce or utilize high-intensity laser pulses. By using metasurfaces (Si on Sapphire) made of sub-wavelength scale structures (Si), optical nonlinearity leading to the generation of high harmonics (up to 11$^{\text{th}}$) was reported at irradiation intensities below 1 TW/cm^2 [12] with 3700 - 3900 nm pump wavelengths (0.335 - 0.318 eV); the bandgap of Si is 1.12 eV. Such intensities are above the perturbative nonlinearity, which occurs for the $10^{-4}-10^{-3}$ TW/cm^2 range for Si. The enhancement and localization of light between Au nanoparticles drive polymerization inside nanogaps [13]. At typical $1-3$ TW/cm^2 intensities, 3D polymerization is achieved in pure cross-linkable resist/resins without photo-initiators by direct writing approaches at sub-diffraction limited feature sizes [14].

1.2. Towards Large Area Patterning

All current solar cells trap light using random micro-textured surfaces; in Si, these are a KOH-etched pattern of random pyramids. With appropriate coating, that random texture contributes to anti-reflection properties. However, the best-performing limit of such light trapping (ray optics) cannot surpass the Lambertian $4n^2$ criterion, where n is the refractive index of the solar cell. We have developed fabrication protocols based on electron beam lithography, projection stepper lithography, and DLW for patterning different mask layers: Cr, Si_3N_4, and AlO_x used for wet and dry plasma etching of Si and Si-on-Insulator surfaces for light trapping beyond the Lambertian limit [11]. The dry

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plasma etch is the most promising approach when the mask is patterned by fs-DLW using Bessel-like beams which have long linear focal region [15]. Plasma etch was simplified for a fast and isotropic etching with a reduced directional bombardment of the surface. After passivation etch with the removal of $\sim$ 300 nm surface layer, the minority carrier lifetime becomes acceptable (a few milliseconds) for actual Si solar cells. In 2023, 23.1% efficiency of light-to-electrical power conversion was achieved using Si solar cells with photonic crystal (PhC) light trapping patterns defined by using Gaussian pulses, which are now changed to Bessel beam fs-DLW [15]. The PhC pattern fabrication for light trapping harnesses the wave nature of light for the enhanced absorption of sunlight by interference. The method is amenable for fabrication over large practical areas up to the panel size ~ 1 m^2.

A large area fs-laser patterning to control surface wetting and anti-icing properties on carbon-fiber-reinforced polymer (CFRP) is another promising field where texturing can be made without damaging fibers [16]. By using the two-liquid (water and ethanol) Owens - Wendt method, it was possible to determine the fs-laser ablated structure with the highest water-repelling property, a super-hydrophobic $\theta_c \sim 159^\circ$ contact angle, for a square pattern (60 μm period with 45 μm width) [17]. The fraction of the textured surface in contact with a liquid can be determined by a graphical method using the Cassie - Baxter equation [18]. A high precision nature of fs-laser ablation is revealed in the ablation of a graphene placed on a sapphire wafer substrate for creating mesh patterns that guide epitaxial lateral overgrowth, facilitating a reduction of dislocations in GaN growth [19].

Here, we reveal the anti-reflective performance of fs-laser patterned metals, including W, Al, and Cu over the near-to-mid IR spectral range. Laser ablation at fluences up to 28 J/cm^2/pulse was orders of magnitude larger than the metal ablation at $\sim 20 \times 10^{-3}$ J/cm^2 with a focal spot of few tens of micrometers. At these conditions, which can be used for large industrial lasers, surface texturing produces nano-to-micro-roughness over several orders of magnitude, from classical ripples of wavelength size to tens-of-micrometers. This hierarchical nature of surface structures was the key of observed low reflectivity $R < 2\%$ over a very broad 1-10 μm IR spectral range. Given Kirchhoff's scaling for emissivity $E = 1 - R$ (in the absence of transmittance T), such surfaces can be used for radiative cooling in the 8-13 μm atmospheric window as well as for heat exchangers, anti-icing surfaces, and the back-side of solar cells including space applications. Such surfaces can be made on different metals and alloys by simple direct laser writing.

2. Experimental: Materials and Methods

2.1. Femtosecond Machining Using Modular Station

A fs-laser setup for large-area 3D machining was assembled by Quoba Systems, delivering 80 W average power at repetition rates up to 2 MHz (1030/515/343 nm, 200 fs) with translational/rotational stages, scanners with theta lens, and fabrication control software.

The laser machining setup, beam delivery, and focusing have been described elsewhere [20]. Such fs-fab stations can be assembled and integrated from separate components, as demonstrated in Ref. [20]. Two high-precision rotational axes are available for a full 5-axis fabrication capability. Integration of high-NA objectives for resolution down to sub-μm fabrication is possible along with the setup of a Bessel beam for high-speed cutting of transparent materials and patterning on non-flat surfaces. An external pulse compressor (n^2 Photonics GmbH, Hamburg, Germany) for 50 fs and 10 fs pulses in one or two stages, respectively, can be used with this setup. The information required to determine processing conditions is repeated in a shortened form to facilitate discussion.

Multi-axis fs-laser CNC micro-machining system is based on fs-laser, high-speed galvanometer scanner, 5-axis sample positioning stages, system control, and software. The 80 W Carbide (Light Conversion) laser with $\lambda = 1030, 515, 343$ nm wavelengths, pulse duration $t_p = 200$ fs, maximum pulse energy of 0.8 mJ, and repetition rate up to $f = 2$ MHz with tunable GHz and MHz burst with burst-in-burst (bi-burst) capability was used. Switching between linear and circular polarization is implemented.

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A telecentric fused-silica F-theta lens (Jenoptic, JENar) with a $F = 160$ mm focal length was used with a galvanometer scanner (Raylase, SUPERSCAN IV). The laser beam diameter $D = 5$ mm. This is defined by the F-number $F_\# = F/D = 32$ related to the numerical aperture $NA = 1/(2F_\#) = 0.0156$. Theoretical diameter at focus $2r = \frac{4\lambda}{\pi} F_\# = 42$ μm while the depth-of-focus is $DoF = \frac{8\lambda}{\pi} F_\#^2 = 2.69$ mm for $\lambda = 1030$ nm. The axial extent of the pulse defined by the pulse duration $ct_p = 60$ μm was much shorter than the axial extent of the focal region. The laser beam quality factor was $M^2 = 1.2$ defining the beam diameter at focus 50.5 μm and $DoF = 3.87$ mm. The F-theta lens focusing produced a beam with diameter $2r = 60$ μm for the entire scanning field of 50×50 mm^2. This value was used for the calculation of fluence and intensity. The focal position was fixed without axial position change during the ablation of deeper patterns.

High precision, direct drive stages (Standa) with non-contact optical encoders ensure high positioning accuracy: 0.5 μm bidirectional repeatability, 1 μm absolute accuracy over the whole travel area of 400×400 mm^2. The acceleration and speed can reach 2 g and 2 m/s, respectively. System controllers (Polaris) were used to synchronize all axes with the laser providing an infinite field of view (IFOV) with split motion tasks between stages and scanners to achieve optimized scanning speed for accuracy and minimal stitching errors.

2.2. Structural and Spectrum Characterizations

Surface structures were captured with scanning electron microscopy (SEM) using the RAITH 150TWO electron beam lithography writer. The ablation volume and depth were measured using a Bruker Contour GT-K 3D Optical Profiler. Fourier transform infrared (FTIR) spectra were measured using a BRUKER Hyperion 1000/2000 Fourier-transform infrared spectrometer equipped with a microscopy unit.

2.3. Elemental and Chemical Binding Analysis

Elemental analysis was conducted on energy dispersive X-ray spectroscopy (EDS) coupled with an SEM to capture surface element profiles (depth sensitivity up to $\sim$ 1 μm). Chemical bonding analysis was conducted using X-ray photoelectron spectroscopy (XPS) with the Kratos Nova XPS (up to 10 nm) on both ablated and non-ablated surfaces. For XPS spectrum analysis, single-peak (singlet) fitting, which does not account for spin-orbit splitting, is generally sufficient to represent most cases. However, when single-peak fitting does not capture all spectral features, doublet fitting, which considers spin-orbit splitting, is employed to provide a more accurate representation. In this research, the copper sample used singlet fitting for Cu 2p peak with binding energy (930-938 eV), and doublet fitting was used for tungsten and aluminum samples for W 4f (30-40 eV) and Al 2p (71-77 eV), respectively. The binding energy positions and their full-width half maximum (FWHM) were determined based on the XPS database [21], and the previous studies on aluminum [22–26] and copper [27–29].

3. Results and Discussion

In this study, we used maximum pulse energies of 0.8 mJ with tailored pulse overlap from 1 to 10 pulses for a large volume ablation exploring different measures of machining efficiency: $\sim$mm^3/pulse, mm^3/s, mm^3/J and conditions when high-quality machining with minimal debris, burr, and melt-flows can be realized. The typical metal ablation threshold of 0.1 J/cm^2/pulse was exceeded up to 30 times. Different metals, including Al, Cu, W, and stainless steel, were surface textured, leading to their black appearance in the visible spectral range. A reflectance $R \leq 10\%$, which is unusually low for metals, was found extending up to $\sim$ 20 μm in the IR spectral region. Patterns of conical holes, with sizes slightly smaller than the focal spot, were observed on processed metals and were most typical on Al (Figure 1). The low reflectance $R \leq 2\%$ over the IR spectral range (1.5-20 μm) was comparable with the high emissivity $E \geq 0.94$ of black body spray-coated samples ($\sim$ 0.2 mm thickness, Tasko TA410KS); $E \equiv A = 1 - R$ for thick samples with $T = 0$. Reflectance spectra in near-mid IR and surface

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appearance shown in Figure 1 with detailed discussion and comparison between ablated surfaces of W, Al, and Cu are given next.

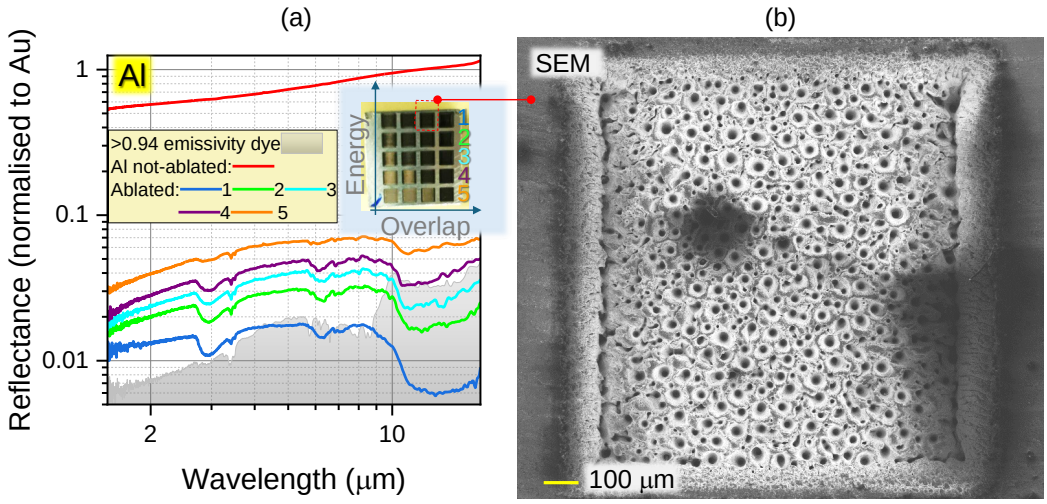

Figure 1. (a) Reflectance of Al after ablation by 1030 nm/200 fs/0.1 MHz irradiation at different scanning speeds corresponding to different in-line separation between pulses $\Delta x = (7-42)$ μm (1-to-5) and different pulse energies $E_p = 0.8$ mJ (1) to 0.16 mJ (5). The focal spot size is ~ 60 μm; the inset photo shows a test matrix of 1×1 mm^2 test fields. Polarisation on the sample is close to circular. The high emissivity $E \geq 0.94$ of black body spray-coated samples with ~ 0.2 mm thickness using Tasko TA410KS dye was used for the reference. (b) SEM image of black-Al with typical surface of low-R in the IR spectral window.

3.1. Ablation with High-Intensity fs-Laser Pulses

Ablation experiments for W, Al, Cu metals with the electron work functions: $w_e = 4.55$ eV (polycrystalline W), 4.06-4.2 eV (Al), 4.48-5.1 eV (different planes of Cu) were performed at the fundamental laser radiation wavelength of 1030 nm with a beam diameter on the surface $2r = 60$ μm. Hatching between adjacent lines was fixed at $\Delta y = 50$ μm, which is slightly smaller than the focal diameter. For the tungsten sample (Figure 2a), the linear beam travel speed was set as $v_{sc} = 1000 - 25$ mm/s along the x-direction at the repetition rate of 100 kHz, producing pulse-to-pulse spacing of $10 - 0.2$ μm. The fluence per pulse was fixed at $F_p = 24.76$ J/cm^2 corresponding to the pulse energy of $E_p = 0.7$ mJ and the pulse duration of $t_p = 200$ fs; the average intensity per pulse is $I_p = F_p/t_p = 123.8$ TW/cm^2. A combination of different pulse spacing with a single pass or 5 passes was performed.

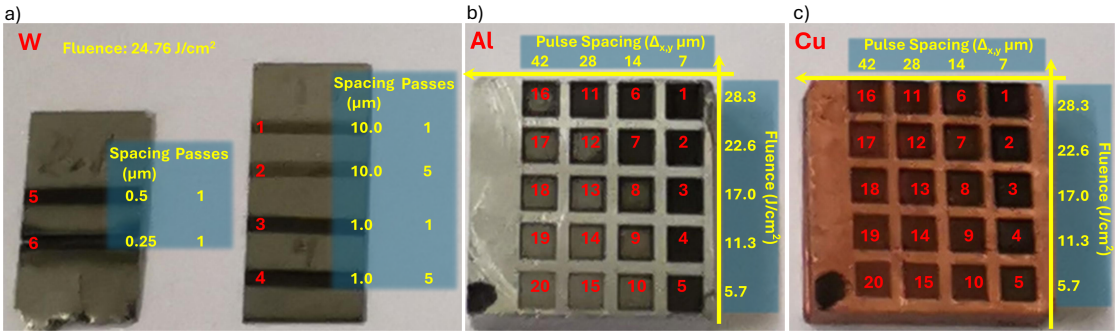

Figure 2. Fs-laser ablation of (a) tungsten with pulse spacing (10 - 0.25 μm) and passes (1, 5), (b) aluminum with pulse spacing ($42 - 7$ μm) and fluence per pulse (28.3 - 5.7 J/cm^2), (c) copper (the same ablation condition as aluminum).

For aluminum and copper (Figure 2b,c), a total of 16 ablation areas were fabricated on each metal coupon's surface, defining the ablation matrix of various pulse spacing $42 - 7$ μm with different

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fluence per pulse 28.3 - 5.7 J/cm^2. Each ablated area, created under specific ablation conditions, was labeled with numbers (W: 1–6, Al: 1–16, Cu: 1–16) to align with the subsequent characterization results (Figure 2).

Tested metals are very different in their physico-chemical properties. The molar enthalpy of vaporization (atomization) of Cu is 300 kJ/mol (338 kJ/mol), for Al 293 kJ/mol (326 kJ/mol), and for W 807 kJ/mol (849 kJ/mol - the highest among chemical elements). The enthalpy of vaporization recalculated per atom is 3.11 eV/atom (Cu), 3.04 eV/atom (Al), and 8.36 eV/atom (W). Solid density of Cu $\rho_{Cu} = 8920$ kg·m^{-3} (molar volume $V_m^{(Cu)} = 7.11$ cm^3 and molar mass $M_{Cu} = 63.546$ g/mol), for Al $\rho_{Al} = 2700$ kg·m^{-3} ($V_m^{(Al)} = \frac{M_{Al}}{\rho_{Al}} = 10$ cm^3 where molar mass $M_{Al} = 26.98154$ g/mol), and for W $\rho_W = 19280$ kg·m^{-3} ($V_m^{(W)} = 9.54$ cm^3 and molar mass $M_W = 183.84$ g/mol).

The ablation threshold for metals can be estimated by Gamaly's model for the pulse fluence [30]. According to it, the ablation is initiated by depositing energy to electrons equal to the material's binding energy and electron work function [30]:

$$F_{th}^{(m)} = \frac{3}{8}(\epsilon_b + w_e)\frac{\lambda n_e}{2\pi}, \tag{1}$$

where ϵ_b is the binding energy or enthalpy of vaporization, w_e is the electron work function (escape energy from a metal), $l_s = c/(\omega\kappa) \equiv \lambda/(2\pi\kappa)$ is the absorption depth (the skin depth) in the plasma with electron density n_e and refractive index $n^* = n + i\kappa$ with c and ω being the speed and cyclic frequency of light, respectively, and A is the absorption coefficient (for good metals $A \approx \frac{2\omega l_s}{c}$). To estimate ablation thresholds, the smallest one of the listed w_e [eV] and binding energy per atom ϵ_b [eV] values were used. The electron density is estimated considering one electron per atom donated to metallic bonding $n_e^{(m)} = N_A/V_m^{(m)}$, where N_A [mol^{-1}] is the Avogadro number and $V_m^{(m)}$ [cm^3] is the molar volume calculated above. With all parameters defined and $\lambda = 1030$ nm, the following ablation thresholds are obtained from Equation (1): 0.40 J/cm^2 (Cu), 0.26 J/cm^2 (Al), 0.34 J/cm^2 (W). These are single-pulse ablation thresholds. As the surface is ablated and reflectivity is gradually reduced with subsequent pulses, the accumulation dose or F_p times the number of pulses N per spot of diameter D: $N = D/v_s/f$ at scanning speed v_s and laser repetition rate f can reach the ablation threshold even at slightly lower pulse energies.

The experiments in this study were carried out at irradiance up to 30-100 times above the threshold, moreover, with up to $N = 10$ pulses per focal spot. Noteworthy, that hard X-rays are generated at such conditions [31] requires the screening enclosure of the sample chamber, especially when multi-pulse or burst modes of exposure are used [32].

3.2. Reflectivity of Laser Ablated Surfaces at IR Spectral Range

The ablated area on W, Al, and Cu samples shows a black appearance in the visible spectral range. The reflectance of these black surfaces was tested at near-to-mid IR range $1.5 - 18$ μm shown in Figure 3 corresponding to the labeled areas on the samples (Figure 2). The IR reflectance shows a clear reduction of reflectance for all ablated metals: $R < 40\%$ (W), $R < 15\%$ (Al), $R < 55\%$ (Cu), compared with the non-ablated surfaces $R \sim 98\%$ (W), $R \sim 90\%$ (Al), and $R \sim 95\%$ (Cu). The anti-reflectance effect is positively related to the energy deposited on metal surfaces, i.e., the higher energy deposition (higher fluence and smaller pulse spacing) produces surfaces with smaller R at the IR window. The lowest reflectance for each sample was $R < 5\%$ (W-6), $R < 3\%$ (Al-1) and $R < 6\%$ (Cu-1) corresponding to a formidable reflectance decrease around 90%. Formation of Al_2O_3 is recognisable by its absorbance around ~ 6 μm in the reflectivity spectra. The so-called water absorption band associated with 3-3.5 μm window is due to Al-OH (a decrease in reflectivity due to absorption).

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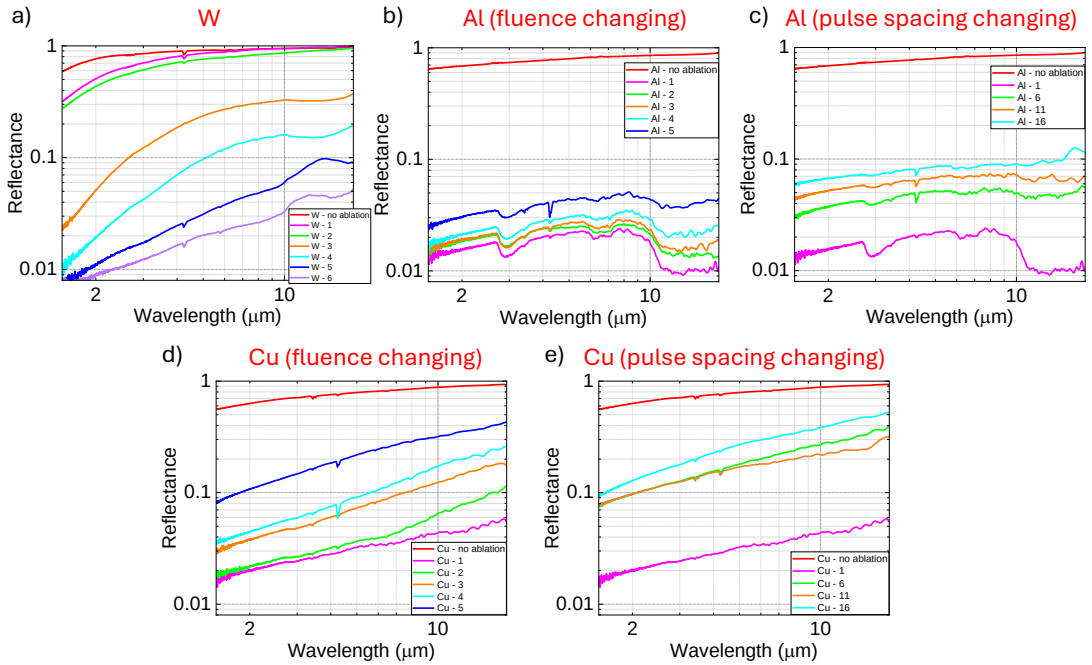

Figure 3. The IR reflectance spectra at the wavelength of $1.5 - 18$ μm for (a) tungsten, ablated with different fluence for the largest pulse-to-pulse overlap $\Delta_{x,y} = 7$ μm; (b) aluminum (ablated with different fluence for the largest pule-to-pulse overlap $\Delta_{x,y} = 7$ μm) and (c) different pulse spacing (at $F_p = 28.3\,\mathrm{J/cm^2}$); copper ablated with (d) different fluence (for the largest pule-to-pulse overlap $\Delta_{x,y} = 7$ μm) and (e) different pulse spacing at $F_p = 28.3\,\mathrm{J/cm^2}$.

Figure 4a,b sumarises the reflectance R over the measured $\lambda = 1.5 - 18$ μm window for the 4×5 matrix of $Spacing \times Fluence$ for Al and Cu. Apparently, the highest fluence at the strongest pulse-to-pulse overlap produced the lowest reflective surfaces for Al and Cu. This corresponded to the largest ablated volume as shown in Figure 4c. For the different $\Delta_{x,y}$ pulse overlaps, a linear scaling of ablated volume $V_{al} \propto F_p$ as well as the depth $H_{ab} \propto F_p$ was observed.

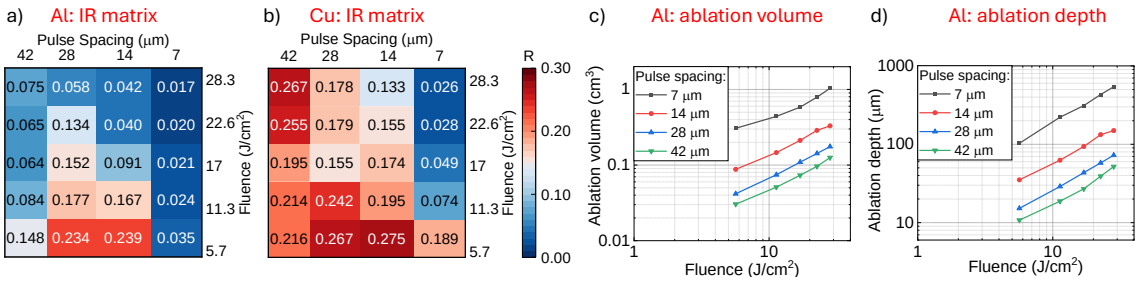

Figure 4. The average reflectance R at $1.5 - 18$ μm spectral window for (a) Al, (b) Cu, corresponding to the labeled areas in Figure 2. (c) The ablated volume and (d) the average ablation depth of Al with the change of pulse spacing and fluence. The ablation volume was calculated as $V = \int\int D(x,y)dA$, where $D(x,y)$ is the local depth function over the measured region, and dA is the infinitesimal area element same as $(dx\,dy)$. The ablation depth is the average value of depth (distance from the bottom of the grove to the xy-plane) along the measured region.

The surface morphology at different magnifications was inspected with SEM and shown in Figure 5 for specific fluence and pulse overlap conditions. Very different surface nano-micro topographies are observed from ripples with a period close to the laser wavelength ~ 1 μm to the structures with dimensions close to the focal spot size of ~ 40 μm. The most anti-reflective pattern on Al (in (b)) had the richest 3D topography. The conical inverted pyramidal structures are apparent as holes on the surface were clearly observed on Al, which has the lowest melting temperature of 660°C compared with Cu (1084°C) and W (3422°C).

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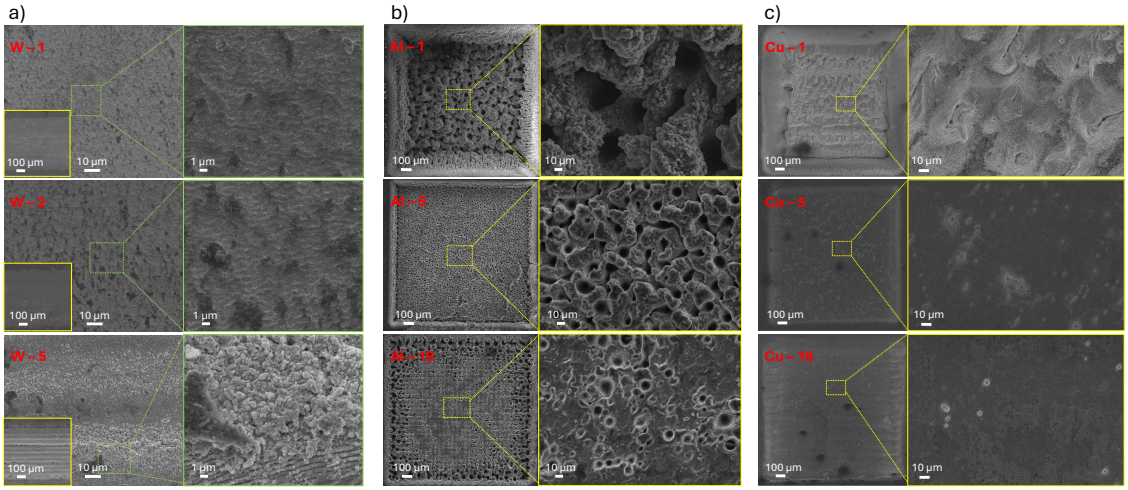

Figure 5. SEM images of laser machined (a) W, (b) Al, and (c) Cu surfaces ablated by 1030 nm/200 fs/0.1 MHz pulses. Sample nomenclature is according to the Figure 2. The W fabricated at the same fluence 24.76 J/cm^2 with the change of pulse-to-pulse spacing and number of passes as W-1: 10 μm & 1 pass, W-2: 10 μm & 5 passes, W-5: 0.5 μm & 1 pass. The Al and Cu were fabricated with the change of fluence and pulse-to-pulse spacing as Al-1& Cu-1: 28.3 J/cm^2 & $\Delta_{x,y} = 7$ μm, Al-5 & Cu-5: 5.7 J/cm^2 & 7 μm, Al-16 & Cu-16: 28.3 J/cm^2 & 42 μm.

The most complex 3D textures were observed on Al, which has the lowest melting temperature among tested metals. The feature size of conical holes in Al is close to the full width at half maximum (FWHM) measure of the focal spot size. The photon pressure exerted by a pulse of irradiance $I_p =$ 100 TW/cm^2 or 10^{18} W/m^2 is $P_{ph} = I_p/c \approx \frac{1}{3} \times 10^{10}$ Pa = 3.3 GPa, where $c \approx 3 \times 10^8$ m/s is the speed of light. This pressure is applied when the fs-laser pulse energy is deposited (absorbed), while the reflection doubles it via the momentum transfer due to the reversal of the photon direction. Hence, the laser peening is present. The imparted pressure is a contributing factor to the formation of surface textures guided by an interplay of Al softening/melting together with fast thermal quenching due to high thermal conductivity.

The structural color effect due to surface morphology is an obvious contributor to the anti-reflective (color-black) appearance at vis-IR spectral ranges. However, the chemical modification of metal surfaces processed in air under ambient conditions has to be assessed as well, especially when it is relevant to very different perspectives of applications. For Al and Cu, which are both very chemically active and were processed at an energy condition exceeding their ablation threshold by more than $\sim$ 30 times, chemical modifications were scrutinized using XPS and EDS as discussed next.

3.3. Surface Chemistry on Surfaces Ablated at Tens-of-TW/cm^2 Fluence

Figure 6 shows XPS spectra at metal-specific binding energy window, which was analyzed by peak fitting and area comparison for quantitative analysis. Tables 1–3 summarise the quantitative XPS results and reveal intricate changes in chemical bonding on the surface of tungsten, aluminum, and copper, respectively, before and after laser ablation.

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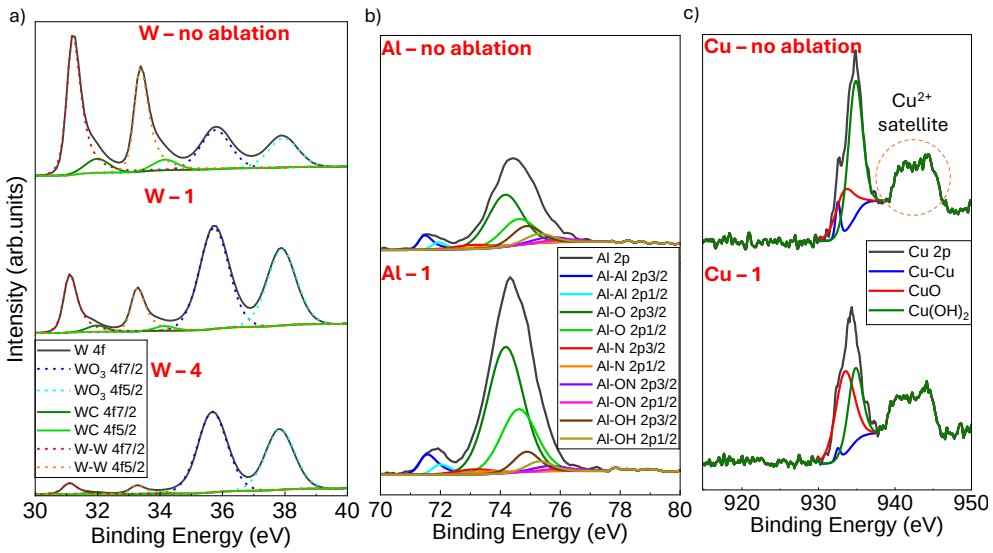

Figure 6. XPS analysis of pristine W, Al, Cu coupons and laser patterned at different conditions (see Figure 2 for marking).

The tungsten sample showed a notable increase in metal oxidation with WO_3 bonding increasing from 30.22% (W - no ablation) to 91.22% (W - 4), and the oxidation is proportional to the amount of energy deposited on the surface (Table 1). This indicates that oxidation was taking place at high-temperature conditions, which is required for inert metal W. Fs-laser pulses engraved nanostructures such as protrusions and ripples on W-metal surfaces, which can be oxidized at elevated temperatures in air [33]. The equation-of-state (EoS) of W from cryogenic to melting temperatures has been recently proposed [34] and can predict the high-temperature and high-pressure response of W.

The ablated aluminum surface showed an increased percentage of Al-O bonding, which is consistent with previous findings [23,35]. The Al-O bonding increased from 61.46% to 76.80% while the Al-OH bonding dropped from 18.01% on pristine Al surface to 8.84% on ablated surface (Table 2). Apparently, the top layer of hydroxide was removed by ablation, and oxidation was prevalent on a nano-micro rough surface with a Al_2O_3 layer well in line with the earlier study [23]. The oxidation might be influenced by two possible mechanisms. One is the oxidation of aluminum due to sample exposure to air after laser ablation. The other is the interaction between aluminum ions in plasma and oxygen with re-deposition onto the sample surface. A very fast oxidation/passivation process of Al takes place at $\sim 1050 - 1150°C$ window, but a distinct incubation time was required for oxidation above $\sim 850°C$ as found in a recent study by differential scanning calorimetry [36]. When Al was preheated to high temperatures with oxygen, the oxidation progresses with the expansion and growth of material, thus different granular structures were formed with thicknesses up to micrometers [36]. The evaporation of Al and initial mass loss in Ar at high temperature was proportional to the Al vapor pressure.

The copper sample shows a strong Cu^{2+} satellite peak around 943 eV, indicating that the oxidation form is the cuprix Cu(II) oxide CuO. The oxidation state of copper was found to be dependent on the ablation conditions, e.g. CuO is formed at a lower beam velocity of 20 mm/s, while Cu_2O tends to form at a higher velocity of 100 mm/s [29]. Similar to the Al surface, laser ablation changed the surface composition of the copper compound, with CuO increasing from 27.57% to 58.80% and $Cu(OH)_2$ decreasing from 66.50% to 39.10% (Table 3). The oxidation of Cu under fs-laser ablation can explain the color (in visible light) appearance of surfaces due to the thin oxide layer [20]. Understanding the laser processing parameters that can control Cu oxide formation on laser-ablated ripples is important for photo-cathode applications [37].

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Table 1. Tungsten sample surface compounds before and after laser ablation.

Sample	WO_3	WC	W-Metal
W - no ablation	30.22	8.78	61.00
W - 1	72.98	3.04	23.98
W - 4	91.22	1.20	7.59

Table 2. Aluminum sample surface compounds before and after laser ablation.

Sample	Al-metal	Al-O	Al-N	Al-ON	Al-OH
Al - no ablation	8.94	61.46	5.44	6.16	18.01
Al - 1	8.19	76.80	3.28	2.90	8.84

Table 3. Copper sample bond information before and after laser ablation.

Sample	Cu-metal	CuO	$Cu(OH)_2$
Cu - no ablation	5.93	27.57	66.50
Cu - 1	2.10	58.80	39.10

High-intensity laser pulses trigger strong thermal gradients, enhancing the oxidation process [38] and metal compounds are shifted towards metal oxides. Oxides are thermodynamically stable and dominate over the formation of hydroxides, carbides, nitrides, and oxynitrides consistent with findings in this study (Tables 1–3). Metal oxides such as Al_2O_3, WO_3, and CuO have a lower refractive index and contribute, in part, to the reduction of reflectance. The 3D textured structure on the ablated metal surfaces also traps light and contributes to the reduction of reflectance.

Elemental analysis was also carried out using EDS. The results are summarised in Table 4. Since EDS determines the elemental composition and is not sensitive to the chemical bonding, as well as probing the larger micrometer-scale depth from which X-rays can escape, the results are different to XPS and have a qualitative character. A surprising observation was the unusual carbon content in as-received Cu coupons, which were cut by a standard mechanical saw tool with oil used as a cooling agent. All samples were IPA washed before experiments; however, only Cu showed C contamination in the EDS measurements. After ablation, only oxygen was detected in addition to Cu. In all W, Al, and Cu samples, metal content exceeded that for the known oxides and O-containing surface compounds. This is expected due to the large micron depth of EDS probing since oxides are on the surface at the nanoscale.

Table 4. Elemental analysis using EDS, according to the K_α lines

Sample	Metal atomic percentage	Non-metal atomic percentage
W - no ablation	W: 100.00%	O: 0%
W - 4	W: 70.57%	O: 29.43%
Al - no ablation	Al: 93.09%	O: 6.47%
Al - 1	Al: 52.92%	O: 46.2%
Cu - no ablation	Cu: 38.63%	O: 8.68% C: 38.63%
Cu - 1	Cu: 72.22%	O: 27.28% C: 0%

3.4. Radiative Cooling Effect of Black Metals

Black (anti-reflective) metal surfaces have great potential for applications in radiative cooling when the low reflectance is in the mid-IR $1.5 - 18$ μm spectral range [39–41]. Physical effects such

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as surface roughness are known to alter emissivity, which is also affected by the surface composition/chemistry [42–44]. Fs-laser texturing is a simple and increasingly practical method to create nano-micro rough textures over large surface areas [20,45]. Such fs-laser-textured surfaces are of interest for catalytic applications [23] not only due to the larger surface area but also due to reduced reflectivity in photo-catalytic applications [46]. Spectrally broad reduction of IR reflectivity demonstrated here can expand the application potential of narrow IR band emitters based on perfect absorbers [47], which can also be made out of high entropy alloys (HEA) [48,49] promising for industrial applications including at high temperature.

Tungsten is a unique material due to its highest melting temperature, very large mass density, chemical inertness, and comparatively low thermal expansion. Its applications can be found from ink spreading ball in a ball pen, served/serves as a lightning filament in incandescent lamps to industry/defense/space industries where surfaces are subjected to extreme temperatures in plane/rocket engines or power plants. The W and WC surfaces with anti-reflective features made by fs-laser texturing can be efficient emitters based on Kirchhoff's law when heated at very high temperatures $\sim 3000^{\circ}$C to cool down surfaces. Moreover, thermal energy harvesting can be more efficient as predicted by Carnot's limit of efficiency $\eta_C = 1 - T_{cold}/T_{hot}$; $T_{cold} = 3$ K at outer space [39]. Thermal radiation harvesting is promising due to its high efficiency [50].

4. Conclusions and Outlook

Laser ablation of the metals W, Al, and Cu by ultra-short 200 fs laser pulses at high 20-120 TW/cm^2 average intensity/irradiance with large focal area (~ 60 μm diameter) produced complex hierarchical 3D surface textures with features ranging from ripples of wavelength ~ 1 μm to inverted pyramidal cones (most typical on Al) with openings of tens-of-micrometers. The most complex 3D textures of the largest height changes were on Al, which has the lowest melting temperature of the metals investigated here. The main chemical change observed in the outer surface layers by XPS was oxide formation. Interestingly, the ablation, which starts as an electron removal from the surface after energy deposition, is synonymous with oxidation, which is the loss of electrons by definition. Ablation at energy deposition up to 100$\times$ times larger than the threshold fluence/intensity facilitates high local temperature, material flow driven by strong thermal gradients, oxidation, and subsequent thermal quenching.

In the context of radiative cooling, oxidation and passivation of metal surfaces are expected to facilitate an increase in thermal emissivity, which is structure and morphology-dependent. Indeed, metals are reflective, and their emissivity is low. The oxide layer and surface roughness, which makes them anti-reflective, are favorable for radiative cooling, especially at elevated temperatures relevant to industrial and space applications. This work has shown that laser ablation with an industrial fs-laser of 80 W power at fast scan can be used to create low-reflectivity surfaces over the 2-20 μm near-mid-IR spectral window.

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