

Niobium as Alternative Material for Refractory and Active **Plasmonics**

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Supporting Information

ABSTRACT: The development of stable compounds for durable optics is crucial for the future of plasmonic applications. Even though niobium is mainly known as a superconducting material, it can qualify as an alternative material for high-temperature and active plasmonic applications. We utilize electron beam lithography combined with plasma etching techniques to fabricate nanoantenna arrays of niobium. Tailoring the niobium antenna geometry enables



precise tuning of the plasmon resonances from the near- to the mid-infrared spectral range. Additionally, the hydrogen absorptivity as well as the high-temperature stability of the antennas have been investigated. Further advantages of niobium such as superconductivity make niobium highly attractive for a multitude of plasmonic devices ranging from active and refractory perfect absorbers/emitters to plasmon-based single photon detectors.

KEYWORDS: refractory plasmonics, niobium nanoantennas, hydrogen, active plasmonics, thermal stability

lasmonic nanostructures^{1,2} are widely used in many optical applications such as nonlinear optics,^{3,4} thermophotovoltaics,⁵ nanoscopic heat transfer system⁶ in photothermal therapy,^{7,8} and plasmonic-based solar cells.⁹ In many applications, highly focused light is absorbed and converted quickly and efficiently into heat.^{10–12} In other devices, structured metamaterials are working as spectrally selective emission sources for thermal radiation.¹³⁻¹

The employed plasmonic materials for the mentioned applications, however, are mainly limited to noble metals such as gold¹⁸ and silver^{19,20} due to their superior optical properties, which enable narrow-band plasmon resonances.^{21,22} While gold exhibits advantageous chemical stability at room temperature when compared to silver, it starts to deform at temperatures above 100 $^{\circ}C^{23}$ unless it is covered with a protection layer.^{24,25} This characteristic can exterminate the plasmonic properties and therefore restricts the use of gold for high-temperature plasmonic applications such as thermophotovoltaics and plasmonics light emitters. Hence, it is necessary to implement alternative plasmonic materials²⁶ that are functional under harsh environmental conditions.^{27,28}

One strategy to overcome the relatively unsatisfactory thermal stability of gold is to use so-called refractory materials for plasmonic applications.^{29,30} These materials are meant to display high chemical stability and are able to withstand very high temperatures due to their melting point above 2000 °C.²⁹ Thus, they can open the door to future high-temperature plasmonic devices. Some materials in this group such as tungsten (W)^{14,31} and molybdenum (Mo)³² have been investigated for plasmonic applications at elevated temperature; however, they suffer from high losses resulting in broad plasmon resonances with low oscillator strength and low field enhancement.^{33,34} Recently, it was found that some transition metal nitrides³⁵ such as titanium nitride (TiN)³⁶⁻³⁸ and zirconium nitride $(ZrN)^{39}$ have very similar optical properties to gold in the near-infrared regime while remaining stable at elevated temperatures.⁴⁰ The disadvantage of these materials, however, is the nonstraightforward preparation methods mostly involving complex reactive processes.⁴¹

Niobium (Nb), which is also associated with the group of refractory plasmonic materials (melting point at 2469 \pm 10 °C), shows similar optical properties to Au and TiN in the near-infrared.⁴² However, unlike TiN, Nb has comparable optical properties to gold in the mid-infrared as well, whereas it shares the high durability of TiN at elevated temperatures. Moreover, Nb has many other interesting characteristics such as superconductivity^{43,44} and hydrogen sensitivity,⁴⁵ making it a very promising material for future plasmonic schemes such as active plasmonic devices⁴⁶ as well as plasmonic-based singlephoton detectors for future quantum computers.^{47,48}

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In this work, we fabricate Nb nanoantenna arrays via electron beam lithography (EBL) combined with plasma etching techniques that enable excellent control over the nanoantenna geometry, resulting in tunable plasmon resonances from the near- to the mid-infrared spectral range. Due to the refractory properties of Nb, the fabricated nanoantennas are suitable candidates for high-temperature plasmonic applications. We investigate the thermal stability of the nanoantennas and their optical properties up to 800 and even 1000 °C. The results confirm the durability of Nb nanostructures, particularly when covered with an oxide-resistant layer such as aluminum oxide (Al_2O_3) .⁴⁹ Furthermore, the hydrogen absorptivity of Nb nanoantennas is demonstrated via in situ spectroscopic observation of the H₂ loading and unloading processes.

RESULTS AND DISCUSSION

The plasmonic properties of any metallic nanostructure are closely associated with the optical properties of thin films from the same material. These properties can be measured using ellipsometry techniques. Figure 1 compares the measured dielectric functions of our Nb thin films with the ones of Au as a noble metal and TiN as the most promising refractory material for plasmonic applications. Generally, negative real and small positive imaginary parts of the dielectric function are favorable for a material to support narrow and well-modulated surface plasmon resonances.⁵⁰



Figure 1. Niobium features high-temperature durability and exhibits plasmonic behavior. (a) Real and (b) imaginary part of the dielectric functions of Nb compared to Au^{51} as a noble plasmonic material and TiN^{37} as another promising refractory metal. Both Nb and TiN were prepared on sapphire substrate with a thickness of 100 nm. Data are extracted from modeled spectroscopic ellipsometry measurements of 100 nm thick films. The inset chart compares the melting points of niobium and titanium nitride that are both chemically stable above 2000 °C (and thus refractory) to the one of gold.

As displayed in Figure 1a, the real parts of the dielectric functions (ε_1) of TiN and Nb are very similar to the one of gold. However, at higher wavelengths (mid-infrared range), Nb has a much smaller ε_1 than TiN and is more comparable to gold, rendering Nb a promising replacement for gold in plasmonic applications in the mid-infrared wavelength range. The comparison of the imaginary parts of the dielectric functions (ε_2) indicates that both Nb and TiN experience comparable propagation losses that are markedly higher than in Au (see Figure 1b).

The higher intrinsic losses of Nb, however, might have some benefits in practical plasmonic applications,⁵² for example, in loss-induced heating with optical tweezers⁵³ or optical data storage systems.⁵⁴ The inset of Figure 1a shows the melting points of Nb and TiN compared to Au, indicating the refractory character of both materials and their possible use for plasmonic applications at elevated temperatures.

The promising optical properties make Nb nanostructures ideally suited for a multitude of applications based on particle plasmon resonances. To achieve precisely defined Nb nanostructures, we combined electron beam lithography with plasma etching to achieve versatile control in the full fabrication process. Figure 2 shows schematic drawings of the Nb nanoantenna fabrication process. The sputtered 100 nm thick Nb film is covered with photoresist (Figure 2a) and exposed selectively via electron beam patterning, resulting in reverse patterns of the desired nanoantennas in the photoresist after a development process (Figure 2b). Via 40 nm electron gun evaporation of Cr (Figure 2c) and a subsequent lift-off process, Cr nanoantennas are produced on the Nb film (Figure 2d). The nanoantennas are then used as etching mask to create the Nb nanoantennas in a plasma etching process (Figure 2e). The remaining Cr is then removed via commercial removal (Figure 2f), leaving bare Nb nanoantennas on a sapphire substrate. Figure 2g shows an exemplarily SEM image of the fabricated nanoantennas. The geometry is well-defined and can be easily tuned in the electron beam exposure process, resulting in a broad tunability of the plasmon resonances.

Broad spectral tunability is a desired feature for many plasmonic applications.^{55,56} Our nanofabrication technique that employs plasma etching and electron beam lithography enables precise control of nanoantenna geometry, resulting in wavelength selectivity of the plasmon resonance from the near-to the mid-infrared spectral range.

Figure 3 shows the transmission spectra of rod-shaped nanoantennas for parallel polarization (E_{\parallel}) with lengths varying from 350 to 800 nm and constant periodicity and width of 1000 and 100 nm, respectively. The results show tunable plasmon resonances from 3800 to 6500 cm⁻¹ with modulation depths up to 90% that increase with increasing antenna length. This effect can be attributed to the enhanced dipole moments, therefore higher absorption and extinction cross sections in the case of longer antennas that reduce the transmittance.⁵⁷ The nanoantenna geometry can also be adjusted to tune the plasmon resonances to shorter wavelengths down to 800 nm (see Figure S1 in the Supporting Information).

Niobium is among the materials that are able to absorb large amounts of hydrogen into their lattice.^{58,59} Due to its exceptionally high hydrogen diffusion coefficient at room temperature ($\sim 8 \times 10^{-10} \text{ m}^2/\text{s}$)^{60,61} and the formation of a compound up to NbH₅, niobium is highly interesting for hydrogen storage applications. The behavior of bulk niobium



Figure 2. Fabrication scheme of Nb nanoantennas: (a) Nb films are prepared via a sputtering process on a sapphire substrate and a layer of photoresist is spin-coated on the Nb film. (b) A subsequent electron beam lithography (EBL) exposure and development processes create an inverse pattern of the nanoantennas in the polymer. (c) Cr evaporation and (d) a lift-off process provide the antenna-shaped mask. (e) The antennas are then transferred to Nb via plasma etching. (f) The remaining Cr is removed by a commercial chemical Cr removal. (g) Exemplary SEM image of a fabricated nanoantenna array (periodicity = 1.5 μ m, L = 700 nm).



Figure 3. Relative transmittance spectra of various nanoantenna arrays (measured in parallel polarization, E_{\parallel}). The fabricated Nb nanoantennas feature well-modulated and relatively narrow plasmon resonances in the near- and mid-infrared spectral range. The lengths (*L*) of the antennas is varied from 350 to 800 nm, while keeping the widths and *x*- and *y*-periodicity of the nanoantennas constant at 100 and 1000 nm, respectively.

hydride has been intensely investigated in the past; ⁵⁹ however, very little investigations on the behavior of niobium hydride on the nanoscale have been carried out so far. To obtain first results on the reaction sensitivity of niobium to hydrogen, we fabricate Nb nanoantenna arrays (antenna length 200 nm) resonant at 1170 nm and load them with 4 vol % hydrogen in nitrogen carrier gas. The niobium nanoantennas are covered with 7 nm palladium which is a versatile catalyst, enabling easy hydrogenation at room temperature and ambient pressures. $^{62-64}$ Figure 4 shows the changes of the transmission



Figure 4. Transmission spectra of Nb nanoantennas. (a) Nb rods (blue line) show a distinct particle plasmon resonance at 1170 nm. The optical properties of the rods change after exposure to 4 vol % hydrogen in nitrogen (red line), where the particle plasmon resonance broadens and shifts to the lower spectral region. Heating the sample to 200 °C shifts the resonance back to higher wavelengths (orange line), however, not quite to the initial position. The second H₂ loading brings the resonance back to the same resonance position as the first loading. (b) Exemplary time trace of the measured transmission. After about 40 min sequential hydrogen exposure, the system is saturated. It can be partially recovered via heating to 200 °C. A 7 nm thick Pd cover layer is used as a catalyst on top of the Nb nanoantennas. Whereas the blue shaded areas indicate the hydrogen loading steps, the white areas show the time that the sample is not exposed to hydrogen, demonstrating that the resonance position can be controlled by cutting hydrogen off while the system remains in a metastable state.

spectra and time trace of the resonance wavelength during a hydrogen loading process. The plasmon resonance (Figure 4a, blue curve) blue-shifts about 120 nm to shorter wavelengths until the hydrogen absorption is saturated (pink dashed-curve) and stays in this position at standard temperature and pressure condition due to the relatively strong H-bonding.

The corresponding time trace is presented in Figure 4b, revealing that the resonance position can be controlled by

cutting hydrogen off, as demonstrated at 1150 and 1100 nm. Due to the strong chemical bonding of H-Nb, hydrogen can not be unloaded at room temperature. Therefore, one can precisely tune the resonance position of the NbH_x antennas by controlling the hydrogen exposure time and pressure. Annealing the sample at about 200 °C (yellow area, Figure 4b) partly breaks the chemical bonding and causes the resonance to shift back about by 100 to 1050 nm (orange curve, Figure 4a). The initial position is not reached, since irreversible processes hinder the antennas to return to their original unhydrogenated state at the applied conditions. A second H₂ loading process pushes the plasmon resonance again to the saturated state (red curve, Figure 4a). The faster reaction time compared to the first loading might be due to the presence of the grown niobium oxide (Nb₂O₅) after the heating process that affects the loading time. Our preliminary experiment shows the capability of Nb nanostructures for active plasmonics application as proven by well controlled tunability of the plasmon resonance by applying different H₂ loading times. This promising preliminary results point toward the need for investigations of Nb plasmonic properties at higher temperatures. Future active plasmonic applications of Nb will benefit also by further extensive investigations of the Nb-H system via in situ measurement with different H₂ concentration during exposure to stronger heating. In addition, it would be worth to investigate the reaction of Nb with various gases for different active plasmonics and sensing applications.

Quality and suitability for applications of any refractory material depend upon its stability at high operational temperature. Similar to other refractory metals, Nb bulk is highly stable at elevated temperatures. In the nanoscale regime, however, the optical properties of some materials are modified at high temperature resulting in a change of the plasmonic behavior of the corresponding nanoantennas.^{14,25}

To demonstrate high temperature stability of Nb nanoantennas, we carefully investigate changes of the plasmonic properties of Nb nanoantenna arrays induced by annealing them at 800 °C. The blue curve in Figure 5 shows the plasmon resonance of an exemplary array of Nb nanoantennas (L =1100 nm) that is resonant at approximately 3.5 μ m (~2860 cm^{-1}). After annealing the sample at 800 °C in vacuum condition for 4 h, the resonance shifts to higher wavelengths $(\sim 4 \,\mu m)$ and the modulation depth decreases to 20% (dashed green curve). Nevertheless, it can still be considered a strong, well-modulated plasmon resonance. The changes in the plasmon resonance is mostly coming from the changes of the Nb optical properties since the geometry of the nanoantenna remain same after annealing (see Figure S2 in the Supporting Information). The resonance position and modulation depth remains stable over time as proven by a second annealing process at the same temperature (orange curve). These experiments (also performed for other samples, see Figure S3 in the Supporting Information) demonstrate that niobium nanonatennas withstand temperatures up to 800 $^\circ \text{C}$ without degradation, when they are annealed once. Increasing the annealing temperature to 1000 °C, however, causes irreversible degradation of the Nb nanoantennas and therefore disappearing of the plasmon resonance (see Figure S4 in the Supporting Information).

The functionality of a plasmonic material such as Nb can be further improved for high-temperature application by introducing a protection layer. We use a thin layer of aluminum oxide



Figure 5. High-temperature plasmonic properties of the Nb antennas on a sapphire substrate. The relative transmittance spectrum of the 1100 nm long Nb nanoantennas (blue curve) undergoes a spectral shift of around 400 nm to higher wavelengths with a decreased modulation depth after annealing at 800 °C in vacuum condition (green curve). The optical properties of the nanoantennas remain unchanged during further annealing steps indicating high-temperature stability of the nanostructures and their corresponding optical properties (orange curve).

as protection layer that can perform this task by preventing the growth of metal grains (see Figures 6 and S5 in the Supporting Information), as suggested by Park et al.¹⁴ It also acts as antioxidation layer for experiments at ambient condition.²⁵



Figure 6. High-temperature stability of Nb antennas protected by 5 nm of Al_2O_3 . The spectral location and modulation depth of the plasmon resonance before annealing (blue curve) remains almost unchanged during two annealing processes at 800 °C in vacuum condition (green and orange curves). Additionally, the covering layer also enables the use of Nb nanoantennas at even higher temperatures, as proven by annealing at 1000 °C, which leads only to a small shift of 200 nm.

Therefore, we deposit 5 nm of Al_2O_3 via atomic layer deposition technique (ALD) onto our antennas and measure the plasmonic properties before and after various annealing steps. Figure 6 shows the transmission spectra of a Nb nanoantenna array (L = 1100 nm) covered with Al_2O_3 that resonates at 3.55 μ m wavelength (blue curve). After annealing the sample at 800 °C in vacuum condition for 4 h, the resonance shifts about 70 nm to higher wavelengths without broadening while keeping the modulation depth constant (green curve). Further annealing at same temperature shows virtually no difference and confirms the durability of the covered Nb nanoantennas (orange curve).

The covering layer also enables the use of Nb nanoantennas at higher temperatures such as 1000 °C. Measuring the optical response of the nanoantenna arrays after annealing them at 1000 °C for 4 h, we find that the modulation depth of the resonance decreases by around 10% and resonance position shifts about 200 nm to higher wavelengths as shown in Figure 6 (red curve). The reduced modulation depth is most likely due to intrinsic oxygen interdiffusion between Al₂O₃ and the Nb antennas. Still, our experiments clearly demonstrate the thermal stability of our Al₂O₃-protected Nb nanoantennas up to 1000 °C. The thin layer of Al₂O₃ can sustain temperatures up to 800 °C and acts as protecting layer. Therefore, one cannot see big changes in the SEM images of nanoantenna before and after annealing. At a temperature around 1000 °C, Al₂O₃ starts deformation that results in growth of the grains on top of the Nb nanoantennas (see Figure S6 in the Supporting Information). The covering process also can increase the quality of poor resonances (originating from poor quality Nb films) by modification of grain boundaries that causes decreasing of the propagation losses of the plasmon^{65,66} (see Figure S7 in the Supporting Information).

Although Nb bulk is supposed to sustain even temperatures up to 2500 °C, this has not yet been proven in the nanoscale regime until now. To demonstrate that, a more detailed study to improve the quality of Nb is suggested. Also, further studies to increase the quality and consequently the stability of Al_2O_3 or other oxide layers would be required.

CONCLUSION

In summary, we utilize electron beam lithography combined with plasma etching techniques to fabricate tunable Nb nanoantennas throughout the near- and mid-infrared spectral range. The intrinsic character of Nb as a refractory material makes such nanoantennas well suited for high-temperature plasmonic applications such as thermo-photovoltaics, thermal imaging, as well as nanoscopic heat transfer systems.⁶⁷ A protective layer of 5 nm Al₂O₃ makes the optical response of the antennas stable to annealing at 800 $^\circ C$ in vacuum condition and still usable at 1000 °C. This indicates that the Al₂O₃ layer greatly improves the thermal stability of our Nb antennas. Due to its simplicity and broad applicability, our method opens the door to refractory plasmonics in the midinfrared. In the future perfect plasmonic absorbers^{62,68} from Nb that are cooled below T_c could be used as single photon detectors over a broad near- and mid-infrared spectral range.

METHODS

Sample Fabrication. In preparation for the fabrication process, Nb layers with a thickness of about 100 nm are deposited via DC sputtering onto a sapphire substrate $(1 \times 1 \text{ cm}^2)$ with a deposition rate of 38 nm/min. For the electronbeam lithography, a two-layer positive resist system (poly-(methyl)methacrylate, 200 and 950 K, Allresist) is spin-coated followed by electron beam exposure (Raith eLine Plus). After development, a 40 nm Cr layer and is deposited by electron beam evaporation. After that a subsequent lift-off process is performed in a commercial *n*-ethyl-2-pyrrolidon (NEP)-based remover (Allresist) to prepare chromium nanorods as an etch mask with the etching selectivity ratio of about 100:1. After reactive-ion etching with Freon (CCl₂F₂) for 2 min and

removal of the chromium nanostructures, periodic Nb nanorod arrays of $100 \times 100 \ \mu\text{m}^2$ are present on the sapphire substrate. Pd films were prepared via electron beam evaporation and etched via argon ion beam etching process (Technics Plasma model R.I.B.-Etch 160, beam current range from 90 to 100 mA, typical etching times 20 s).

Optical Measurements. The optical properties of the nanoantennas were measured using a Bruker Hyperion 2000 IR microscope (Schwarzschild-objective with 15-fold magnification, NA = 0.4) coupled to a Bruker Vertex 80 spectrometer with an optical path purged with nitrogen. For the hydrogen-dependent measurements, the sample is mounted in a custom-made vacuum-tight gas cell connected to Bronkhorst mass flow controllers that regulate and monitor the hydrogen and nitrogen gas flows during the measurement with very high accuracy (0.5% Rd).

The dielectric function of the Nb films used in our fabrication process (thickness 100 nm) is measured via spectroscopic ellipsometry (Woollam variable angle spectroscopic ellipsometer (VASE), spectral range 0.3 to 2.2 μ m, angles of incidence varied from 45° to 65° in steps of 5°). The ellipsometric data are modeled by a general oscillator layer model with a mean square error of 0.7. The real and imaginary parts of the dielectric function were extrapolated from the model into the mid-infrared range.

Annealing. The samples were annealed at various temperature in a vacuum glass tube (10^{-6} mbar) with a ramping rate of 10 °C/min to the desired temperatures. Annealing in ambient condition results in oxidation of the Nb and therefore elimination of the plasmon resonance.

Scanning Electron Micrographs. The scanning electron micrographs were acquired with an S-4800 scanning electron microscope (Hitachi Company).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsphotonics.8b00530.

Relative transmittance spectra of various nanoantenna arrays with antenna lengths varied from 150 to 400 nm; high-temperature plasmonic properties of the Nb nanoantennas for a second sample, plasmon resonance of a noncovered sample annealed at 1000 °C; SEM images of the non-covered and covered samples before and after annealing (PDF).

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

Au, gold; W, tungsten; Mo, molybdenum; TiN, titanium nitride; ZrN, zirconium nitride; Nb, niobium; Cr, chromium; Pd, palladium; Al₂O₃, aluminum oxide; N₂, nitrogen; H₂, hydrogen; SEM, scanning electron microscope; EBL, electron beam lithography; ALD, atomic layer deposition; T_c , superconducting transition temperature; Rd, accuracy as a percentage of reading

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