Multilayer tungsten-alumina-based broadband light absorbers for high-temperature applications

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Abstract: Efficient broadband absorption of visible and near-infrared light by low quality-factor metal-insulator-metal (MIM) resonators using refractory materials is reported. Omnidirectional absorption of incident light for broad angles of incidence and polarization insensitivity are observed for the fabricated MIM resonator. Excellent thermal stability of the absorber is demonstrated at high operating temperatures (800 °C). The experimental broadband absorption spectra show good agreement with simulations. The resonator with 12 nm top tungsten and 100 nm alumina spacer film shows absorbance above 95% in the range of 650 to 1750 nm. The absorption window is tunable in terms of the center wavelength, bandwidth, and the value of maximum absorbance (~98%) by simple variation of appropriate layer thicknesses. Owing to their flexibility, ease of fabrication and low cost, the presented absorbers have the potential for a wide range of applications, including the use in commonly used infrared bands or absorbers for (solar) thermo-photovoltaic energy conversion, where high absorbance and simultaneously low (thermal) re-radiation is of paramount importance.

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1. Introduction

Recent development in the fields of thermo-photovoltaic (TPV) energy conversion, solar energy harvesting, photo-detectors, and thermal imaging and emission has highlighted the significance of broadband absorbers [1–8]. The ideal blackbody absorber possesses an absorption magnitude equal to unity and omnidirectional, polarization-independent nature [9, 10]. Several methods have been developed to obtain broadband absorption, such as lattice-scattering effects, excitation of slow-light modes, impedance matching, multiple resonances and adiabatic nano-focusing of gap surface plasmon modes [11–14]. However, the fabrication process of these absorbers includes electron beam lithography or focused ion beam milling that is expensive, time-consuming and only feasible for fabricating over a few 100 $\mu$m$^2$ area, which limits their applicability. Significant progress has been made over the last years in achieving broadband absorption with continuous metal-insulator-metal (MIM) resonators based on chromium, gold, titanium and silicon dioxide materials, by simple, cost-effective wafer-scale fabrication methods [15–17]. The broadband absorption window of these resonators can be improved further by increasing the number of metal and dielectric film layers; however, there is a severe trade-off between omni-directionality and absorbance. Moreover, multilayered resonators require increased fabrication cost and time, while leading to a decrease in the high-temperature stability. It is worth pointing out that the geometry and entailing physics of the resonators described in this work differ substantially from equally named MIM resonators supporting so-called gap-surface plasmons.

Although the MIM resonators provide broadband absorption, their melting points (for thin metal layers) are rather low because of the relatively low melting points of the bulk materials combined with the grain sizes of the thin metal layer causing melting point depression [18, 19]. In particular, the efficient application in TPV/solar TPV energy conversion requires that the absorber is capable of withstanding high operating temperatures. Achieving both angular and polarization insensitivity in a broadband absorber with high-temperature stability by an MIM resonator remains a challenge. In this regard, refractory materials can improve the limiting temperature instability of thin films. Therefore, tungsten and alumina [with bulk melting points of 3422 and 2072 °C, and low thermal expansion coefficients of $4.2 \times 10^{-6}$ and $5.4 \times 10^{-6}$ m/(m·K) at room temperature, respectively] are used in the present study to fabricate the MIM resonator. Tungsten is a good radiation absorber in the visible range since the real part of the dielectric permittivity is positive below 900 nm, while the imaginary part is significant. A rather large imaginary part (in comparison with the real part) of the dielectric function of tungsten results directly in efficient light absorption by metallic layers of the resonator, which allows one to minimize the reflection from the (opaque) resonator as well as usually occurred near-infrared heat radiation (thermal re-radiation) at high temperatures [20–22]. The absorption spectrum of a 100 nm thick tungsten film exhibits a substantial drop in absorption from 47% to 18% when tuning the wavelength from the visible to near-infrared [Fig. 1(c)] due to impedance mismatching between free space and tungsten (that becomes progressively a better metal for longer wavelengths).
A high melting point in conjunction with a low thermal expansion coefficient makes tungsten a promising material for broadband absorption at high temperatures [23]. In addition, a protective coating (PC) of alumina can be deposited over the MIM structure to stabilize the film at high temperatures and to widen the absorption band [24–26]. Herein, we report fabrication and characterization of a tungsten and alumina based MIM resonator as a broadband absorber working in the visible and near-infrared. The absorption window can be tuned in the visible and near-infrared spectral regions by varying the dielectric layer thickness, and - to a significantly lesser extent - by varying the top metal layer thickness, which influences the reflection phase of the mode propagating inside the dielectric layer. The maximum absorbance of the resonator is optimized by variation of the top metal and protective coating film thicknesses. Experimental absorption spectra show good agreement with theoretical calculations. The broadband absorption for both transverse electric (TE) and transverse magnetic (TM) polarizations is high at normal incidence light, and remains to be high at angles of incidence of up to 50°. The high-temperature stability of the substrate is examined by annealing the resonator for 4 hours at 600 °C in air and 800 °C in vacuum. A secondary-ion mass spectrometer is used for compositional analysis of the resonator interfacial layers. It should be pointed out, that the absorber could straightforwardly be adapted to function in commonly used infrared bands, such as e.g. the 3-5 μm band.

2. Method

2.1. Fabrication

The broadband absorbers are fabricated on a polished silicon [p-type, C-Si(100)] substrate using e-beam deposition (for alumina) and DC sputtering (for tungsten) at a rate of 0.3 Å/s. First, a 30 nm alumina followed by a 100 nm thick tungsten layer are deposited on a silicon substrate, where alumina works as an adhesion promoter between the silicon substrate and a tungsten layer. Subsequently, tungsten and alumina layers of
desired thicknesses are deposited. Cross-sectional SEM images are taken by a Zeiss 1540 XB machine.

2.2 Optical measurements

Reflection measurements in the visible and near-infrared regions are performed on a PerkinElmer Lambda 1050 spectrometer with a 150 mm integrating sphere. Reflection measurements are taken with a wavelength scan step of 3 nm and normalized to a labsphere spectralon reflectance standard. The oblique angle of incidence spectra are measured with a variable angle reflectance center mount holder, which is attached to the integrating sphere. For mid-infrared measurements, a PerkinElmer Spectrum One FTIR spectrometer is used. Spectroscopic, variable angle ellipsometry is used (J.A. Woollam, V-VASE ellipsometer) to obtain the optical data (300-2200 nm) for the deposited Tungsten film, while the optical data used for aluminum oxide is interpolated from data presented in [27].

2.3 Simulations

The shown simulation of spectral absorption, field intensity (|E|^2) and local absorption are obtained analytically by use of the thin-film transfer-matrix method [28]. The local field intensity and local absorption are renormalized to their respective maximum values.

2.4 SIMS

A Hiden analytical SIMS workstation is used to analyze the MIMPC resonator. Cesium ions (at 5 keV and 100 nA) are used to sputter the thin film layers and secondary cesium tungsten clusters are detected from an area of 0.3 μm² using an EQS quadrupole analyzer.

Fig. 2. The calculated contour plots of electric field intensity (a) and absorbed power (b) for the resonator (spacer and protective films of a 100 nm Al₂O₃, and a 12 nm top tungsten film) as a function of wavelength and depth into the sample.
3. Results and discussions

The investigated configuration of an MIM (tungsten-alumina-tungsten) resonator with a protective coating layer of alumina is shown in Fig. 1(a). A 30-nm-thin alumina layer (not shown) is used as an adhesion layer between the silicon substrate and a thick tungsten layer. The resonator consists of a 100-nm-thick tungsten layer that works as a mirror (back reflector) and a 12-nm-thin top tungsten layer, acting as a semi-transparent mirror, with the lossless dielectric layer (alumina) functioning as a spacer between the thick and thin tungsten layers. This configuration forms thereby a low-quality factor asymmetric Fabry-Perot (FP) resonator [29]. A cross-sectional scanning electron microscope (SEM) image of an MIM resonator with a protective layer (MIMPC) and a 100 nm alumina spacer layer is shown in Fig. 1(b). The normal-incidence absorption spectra for MIMPC resonators with 30-, 50-, 100- and 150-nm-thick alumina spacer films and 12-nm-thin and 100-nm-thick top tungsten and PC films, respectively, are measured by a UV-Vis-NIR spectrometer [Fig. 1(c)]. The optical absorption is deduced by $A = 1 - R - T$, where $A$, $R$ and $T$ are absorbance, reflectance and transmittance. Since $T = 0$ for an optically thick (100 nm) tungsten layer, the absorption is directly related to the reflection: $A = 1 - R$. Corresponding simulated spectra are calculated analytically using the transfer-matrix method, Fig. 1(d) [28]. For a 100-nm-thick alumina spacer, the resonator exhibits above 95% absorbance in the wavelength range from 650 to 1750 nm and 90% from 625 to 2030 nm, with a maximum absorbance reaching 98% at 750 nm. Broadband spectral tunability across the visible and near-infrared with unchanged high absorbance is demonstrated as the alumina spacer thickness is varied. When de- or increasing the alumina spacer thicknesses to 30 and 50, and 150 nm, a respective blue- or red-shift in the absorption window occurs due to changes in the FP cavity length. Theoretical spectra show good correspondence with experimental spectra, Fig. 1(d).

The absorbance of MIMPC resonators in the mid-infrared region, as measured by an FTIR spectrometer is shown in the inset of Fig. 1(c). The spectral region between 2200
and 3000 nm is not accessible by our experimental setup. The suppression of absorbance (to 0.06 for 50 nm alumina layer) at wavelengths from 3 to 7.5 μm, means that low radiative losses are to be expected when operating at high temperatures. In (solar) TPV systems absorbers are thermally coupled to the emitters. The absorber transmits the absorbed power conductively to a narrow-band emitter, which then emits selectively at a wavelength matched to the bandgap energy of a photovoltaic cell [30, 31]. This scheme does require the MIMPC absorber to have high thermal conductance, which restricts the choice of dielectrics. Re-radiative losses from the absorber are a major limiting factor in TPV efficiency [32, 33], therefore it is necessary to minimize the emission in the spectral range, where the blackbody radiance at the working temperature attains significant values; at 600 °C and 800 °C the blackbody radiation is most intense at 3320 nm and 2700 nm, respectively. Due to the broadband nature of Planckian radiation, it is advantageous to have low absorbance at all wavelengths that do not significantly contribute to the absorption of solar radiation – ideally at all wavelengths larger than the desired absorption window. As such, the low absorbance of the MIMPC resonator at wavelengths between 3 and 7.5 μm strongly underlines its potential for TPV applications. The MIMPC absorbers show a remarkable degree of tunability. For a resonator with a 30 nm alumina spacer film, the absorption window spans from the UV to infrared regions, which can be directly employed to the solar TPV/solar thermal systems. The normalized AM1.5 solar spectrum is shown in the Fig. 1(c) for reference. Since elevated working temperatures are required for solar TPV, the low emittance at a wavelength where significant thermal emission can occur, and high absorption covering most of the solar spectrum of the 30 nm alumina spacer resonator, makes it an ideal candidate for solar TPV applications. Moreover, due to a high absorption of the 150 nm resonator around 2 μm region, it can be used as a blackbody radiator. By varying the spacer film thickness, it is possible to tailor the absorption window for TPV/solar TPV applications or other application where high absorption(emission) is desired in a broad spectral band.

The simulated contour plots of total electric field intensity and absorbed power as a function of wavelength and thickness for a typical resonator with a 100-nm-thick spacer film are shown in Figs. 2(a) and 2(b), respectively. A decrement in field intensity inside the spacer layer confirms the low-quality factor of the resonator; see Fig. 2(a). As seen in Fig. 2(b) the top W layer absorbs most of the incident power in a broad range of wavelengths (above a wavelength of 500 nm), while less dissipation of power occurs in the thick W layer that acts as a mirror reflecting the incident light. The effects of varied top metal and PC film thicknesses on the absorption spectrum are examined experimentally, Figs. 3(a) and 3(c), and by transfer matrix calculations, Figs. 3(b) and 3(d). The broadband absorption spectra are shown for top tungsten film thicknesses of 3, 6, 9, 12 and 15 nm while keeping constant thicknesses (100 and 50 nm, respectively) of PC and alumina spacer films, Fig. 3(a). For 3- and 6-nm-thin top tungsten films, a narrow band around 480 nm with an absorbance of 96% and a wide band around 1220 nm with 76% absorbance are clearly seen. The narrowband absorption around 480 nm is due to the formation of discontinuities in the tungsten film at ultra-low metal thicknesses [34]. In the case of a 9-nm-thin top tungsten layer, absorption lies above 90% at wavelengths from 530 to 1510 nm, with a maximum absorbance of 97%. The absorbance reaches its maximum value (98% at 650 nm) for a 12-nm-thick top tungsten layer, and absorption above 90% is attained in the wavelength range spanning from 530 nm to 1640 nm. In the case of 15-nm-thick and thicker top tungsten films, the bandwidth of high absorption reduces due to the fact that light can no longer penetrate the top layer with sufficient amplitude to be couple critically to the resonator.
For the resonator without a PC layer, Fig. 3(c), wide-band absorption around 800 nm with a maximum absorption of 84% is observed. In the case of a 50-nm-thick PC film, a blue-shift in the absorption band along with a decrement in the bandwidth is seen. For a 100-nm-thick PC film, a maximum absorbance of 98% around 650 nm is obtained, with broadband absorption above 90% occurring in the wavelength range from 530 to 1640 nm. A change in the absorption bandwidth, as well as absorbance, is seen for the PC layer thickness of 150 nm. In general, unitary absorption can be obtained only when the optical impedance of the absorber is matched with the impedance of the medium from which the light is incident on the absorber [17, 35–37]. When the impedance matching condition is fulfilled, all reflections from the resonator cancel out, and the resonator completely absorbs incident light. This amounts to the condition that the decay of the mode in the resonator has equal rates for Ohmic decay and decay to freely propagating modes, respectively [38–40]. The optimal thicknesses of the top tungsten and PC layer for maximum absorbance in the visible and near-infrared spectral regions are 12 and 100 nm, respectively.

For the resonator with a PC layer, Fig. 4, absorption spectra of the MIMPC resonator for 50 nm alumina spacer film with the different oblique angles of incident light (0°-60°) for TE (a) and TM (b) polarization. For the resonator without a PC layer, Fig. 3(c), wide-band absorption around 800 nm with a maximum absorption of 84% is observed. In the case of a 50-nm-thick PC film, a blue-shift in the absorption band along with a decrement in the bandwidth is seen. For a 100-nm-thick PC film, a maximum absorbance of 98% around 650 nm is obtained, with broadband absorption above 90% occurring in the wavelength range from 530 to 1640 nm. A change in the absorption bandwidth, as well as absorbance, is seen for the PC layer thickness of 150 nm. In general, unitary absorption can be obtained only when the optical impedance of the absorber is matched with the impedance of the medium from which the light is incident on the absorber [17, 35–37]. When the impedance matching condition is fulfilled, all reflections from the resonator cancel out, and the resonator completely absorbs incident light. This amounts to the condition that the decay of the mode in the resonator has equal rates for Ohmic decay and decay to freely propagating modes, respectively [38–40]. The optimal thicknesses of the top tungsten and PC layer for maximum absorbance in the visible and near-infrared spectral regions are 12 and 100 nm, respectively.

Fig. 5. Broadband absorption spectra due to specular and specular plus diffusive (total) reflections, taken from a resonator with spacer, top tungsten and PC layer thicknesses of 50, 12 and 100 nm, respectively.
To demonstrate the angle and polarization-insensitive absorption of the MIMPC resonator, we perform absorption measurements on the resonator with both TE and TM polarization, Figs. 4(a) and 4(b), respectively, for oblique angles of incidence. The angle of incidence is varied up to 60° in steps of 10° for the MIMPC resonator with a 50-nm-thick alumina spacer, 12-nm-thin top tungsten and 100-nm-thick PC films. In the case of TE polarization, Fig. 4(a), the MIMPC resonator exhibits a maximum absorption of 98% at angles of incidence of up to 50°. The broadband absorption starts decreasing at the angle of 60°, but remains above 90% over a broad spectral range with a maximum absorbance of 96%. Since the total thickness of the resonator is on the sub-wavelength scale, the accumulated phase change in the resonator due to propagation is small and depends to a large extent on the reflection and transmission phases [41]. Thus, the MIMPC resonator exhibits absorption over visible and near-infrared regions of the spectrum in a broad range of angles of incidence. The absorption loss at higher incident angles is due to the change in the increased path length of the incident light. The angle-dependent absorption spectra of the MIMPC resonator for TM polarization is shown in Fig. 4(b). The spectra show broadband absorption response similar to the TE polarization except for angles of 50° and 60°, where a significant change in absorption bandwidth and a decrease in absorbance in the near-infrared is observed. The absorption spectra were taken by a Perkin Elmer UV-vis-NIR spectrometer equipped with an integrating sphere, which has a minimum angle of incidence of 8° for the reflection measurements. Thus, the total absorption spectra contain both specular and diffuse reflections. A custom-made setup is used to measure the absorption spectrum due to specular reflection [42, 43]. The absorption spectra taken on an MIMPC resonator with a 50 nm alumina spacer, 12 nm top tungsten and 100 nm PC films for specular and, specular plus diffusive reflections are shown in Fig. 5. A good correspondence is observed between the absorption spectra obtained from the specular and total reflection measurements, which indicates that the layer quality is good and does not lead to significant scattering of the specularly incident beam.
The thermal stability of the MIMPC resonator is examined by annealing a resonator with a 50 nm alumina spacer, 12 nm top tungsten, and 100 nm PC films up to 650 °C in air and 850 °C in vacuum, both for a duration of 4 hours. The temperature is ramped at a rate of 8 °C min\(^{-1}\). A blue-shift in the absorption band is observed for the substrate annealed in air at 600 °C in comparison to the non-annealed substrate, see Fig. 6. Since the tungsten and alumina films are deposited at room temperatures, annealing at 600 °C can induce intrusive stresses in the thin layers that can lead to minor degradation of the resonator, which, however, maintains high absorbance over a broad spectral region which is comparable in width, and maximum absorbance to the non-annealed absorber. After annealing at 650 °C in air, a noticeable change in the absorption is seen due to the structural change of the resonator due to oxidation, which is avoided by use of the resonators in vacuum or surrounded by inert gas. Since, solar TPV systems operate in vacuum [32], the upper limit of working temperature of MIMPC resonators are tested with vacuum annealing procedure. Similar to the substrate annealed in air, a comparable blue shift in the absorbance band is observed for the substrate annealed at 800 °C in vacuum. In order to test the thermal cycling stress, the substrate is annealed second time at 800 °C which leaves the absorption spectrum entirely unchanged (Fig. 6), confirming the stability and durability of the absorber against thermal cycling stress at high working temperatures. Substrate degradation starts appearing at 850 °C, resulting in changes to the absorbance and bandwidth of the resonator. In order to investigate the structural changes of annealed substrates, a secondary-ion mass spectrometer is used. A typical compositional analysis of secondary ions of W plotted against the depth of the MIMPC resonator as fabricated, annealed in air at 600 °C and in vacuum at 800 °C, is shown in Fig. 7(a). In the case of vacuum annealing at 800 °C, a very low intensity of secondary ions of W throughout the spacer film confirms a low diffusion rate of tungsten into the adjacent alumina layers, whereas the air-annealed substrate at 600 °C shows a higher percentage of tungsten into the alumina layers due to oxidation. A comparison of samples that were annealed at 800 °C and 850 °C by SEM [Figs. 7(c) and 7(d)] shows a degradation of top W film due to the onset of percolation of the film, when raising the temperature significantly above 800 °C. This may be minimized by using other refractory dielectric materials (with higher melting points), such as magnesium oxide, hafnium oxide, etc., deposited by atomic layer deposition [44] which could be the focus of future work.
4. Conclusions

In conclusion, we have demonstrated an omnidirectional and polarization-insensitive broadband absorber, which is based on the refractory materials tungsten and alumina allowing for high-temperature applications. We show that the structure is stable at 800 °C, in terms of both optical properties and composition. The MIMPC resonator is fabricated using inexpensive and widely available film-deposition techniques, which allows wafer-scale processing of practical broadband absorbers. The development of broadband absorbers suitable for operation at temperatures of up to 800 °C and above has a significant positive impact on a range of practical applications, including TPV systems, solar TPV and solar thermal energy conversion. The tunable bandwidth, variable center wavelength, high absorbance, omnidirectionality, polarization-insensitivity and thermal stability of the resonator makes it an ideal absorber for, amongst others, (solar) TPV applications or as an absorber in commonly used infrared bands. Our findings will help accelerate the adoption of specifically tailored broadband absorbers in efficient thermal systems.

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