Plasmonic thermal IR emitters based on nanoamorphous carbon

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(Received 9 September 2008; accepted 5 February 2009; published online 20 February 2009)

The development of plasmonic narrow-band thermal mid-IR emitters made from a conducting amorphous carbon composite is shown. These IR emitters have greatly improved thermal and mechanical stability compared to metallic emitters as they can be operated at 600 °C in air without any degradation in performance. The emitted thermal radiation has a bandwidth of 0.5 μm and can be set to the desired wavelength from 3 to 15 μm by changing the surface periodicity. The periodically patterned devices have in-band emissivities significantly exceeding that of the non-patterned devices, constituting simple yet efficient radiation sources at this important wavelength range. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3089225]

The middle-infrared (mid-IR) spectral range (from 3 to 15 μm) is of critical importance for thermal imaging, sensing and spectroscopy of chemical and biological agents, and environmental monitoring.[1] Unfortunately, very few radiation sources exist in this range and they are mostly in the development phase. Previously, narrow-band thermal radiation in the mid-IR from metallic photonic crystals and plasmonic two-dimensional (2D) structures was shown.[2–9] Three-dimensional metallic photonic crystals are difficult and costly to fabricate, making 2D structures attractive alternatives. Plasmonic thermal emitters (PTEs) based on periodically patterned metallic films provide tunable, narrow-band radiation, much narrower than from a black-body at the same temperature, constituting a simple yet efficient alternative to costly and complex light sources in the mid-IR. The metallic films typically used in PTEs are prone to oxidization and structural damage at high temperatures. As a result, current metallic PTEs cannot be operated above 350 °C, reducing the maximum achievable output power and limiting the emitted wavelengths to the long part of the mid-IR. In addition, metallic films exhibit very high internal stresses that prevent the fabrication of free-standing membranes, resulting in slow switching (heating/cooling) and low power efficiency due to the large thermal mass of the substrates typically used to support these metallic films. Here we show the development of PTEs made from a highly conductive diamondlike (DL) material called nanoamorphous carbon (NAC) that overcomes these limitations, with significantly improved thermal and mechanical stability compared to their metallic counterparts. The emitted radiation has a bandwidth as small as 0.5 μm and can be tuned to the desired wavelength by changing the periodicity of the surface pattern, constituting an efficient and low cost radiation source in the mid-IR.

DL materials consist of carbon networks characterized by a high relative ratio of carbon in sp^3 states to sp^2 states and have important uses in applications that require high wear resistance, high temperature stability, large dielectric constants, and biocompatibility.[9–13] NAC is classified as a DL material; however, it contains two distinct structural networks: a carbon network that also contains hydrogen atoms and a second network formed by silicon oxides.[14–16] The two networks penetrate and stabilize each other, preventing crystallization. In addition, the presence of silicon oxides results in the high surface smoothness. NAC does not graphitize after heat-treatment of up to 900 °C. It can be heavily doped with metals up to 50 at. %, and the metal resides as nanoclusters in the carbon/silicon oxide network.[17] Pure NAC is an excellent insulator, but doping with metals such as tungsten results in 12 orders of magnitude increase in the conductivity at 30 at. % metal doping.[17] The incorporated metal atoms reduce the inner stress of the doped NAC films, resulting in further mechanical stability.[18]

The abovementioned qualities make NAC films a viable candidate for use in thermal IR emitters, and broadband black-body sources based on NAC are already commercially available.[17] To be suitable for narrow-band PTEs, however, NAC compositions need to satisfy certain requirements. First requirement is high reflectivity, but the intrinsic high emissivity of pure NAC results in small reflectivity in the IR. Furthermore, NAC films need to be periodically patterned with holes at the scale of the emitted wavelength (a few micrometers) to achieve plasmonic narrowing of the thermal radiation, but their chemical inertness and mechanical hardness prohibit the use of conventional micropatterning techniques such as wet etching and lift-off. We have developed an amorphous carbon composite by doping NAC with titanium nitride (TiN)—a very hard conductive ceramic—to achieve high electrical conductivity and IR reflectivity and used plasma-based etching methods to fabricate micropatterned PTEs from these films. NAC films were deposited by plasma-enhanced chemical vapor deposition (PECVD) using suitable silicon-organic precursors[14–18] and were doped with TiN using reactive magnetron sputtering. The deposition rate linearly increases with the magnetron power, and the metal doping results in the control of electrical conductivity of the films over a very wide range [Fig. 1(a)]. The incorporation of the metal results in a sudden large reduction in the specific resistance from well above 100 Ω cm (no doping) to below 10^{-3} Ω cm. Ti contributes to the conductivity through its unbounded form and through various bonds it makes with existing elements in NAC, as evidenced by XPS analysis

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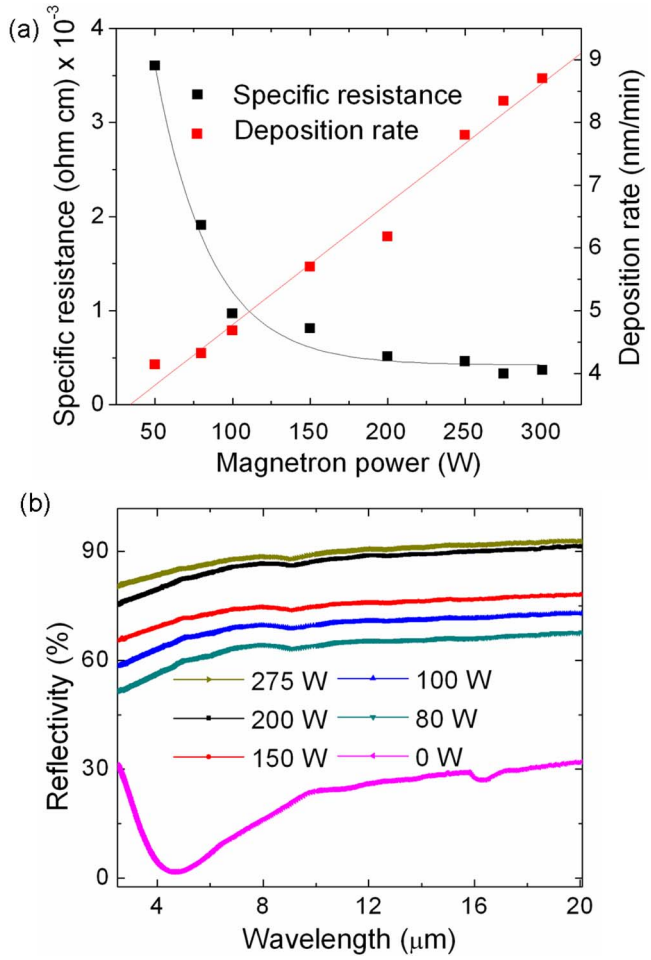

FIG. 1. (Color online) (a) The specific resistance and deposition rate as a function of magnetron power used during PECVD sputtering. The specific resistance data fit well to a first order exponential decay curve (black line). (b) Reflectivity vs wavelength for various TiN:NAC compositions and magnetron power.

showing the formation of Ti–O, Ti–N, Ti–C, and Ti–Si bonds.

The increased electrical conductivity results in an increased optical reflectivity [Fig. 1(b)], and it can be fine tuned with the adjustment of the metal doping, which is controlled by the magnetron power (P). Fourier transform IR (FTIR) spectroscopy measurements show nearly 90% reflectivity around 7 μm for heavily doped films (P=275 W), compared to less than 30% for pure NAC (P=0). The TiN doping removes a large dip in the reflection around 4.5 μm and brings the reflectivity of the NAC in the near-IR range to acceptable levels for use in PTEs.

So far, the highest operating temperature for metallic PTEs has been around 350 °C with the help of special protective coatings. Operation at higher temperatures is needed to obtain larger optical power. In addition, the metallic thin films (i.e., Al, Au, and Ag) used in previous plasmonic IR emitters suffer from very high internal stress, resulting in the necessity of using thick supporting substrates to provide mechanical stability. The use of supporting structures results in increased power consumption and limit switching speeds to around 5 Hz due to the increased thermal mass.[7] We have used TiN doped NAC to overcome these limitations and fabricated narrow-band mid-IR thermal emitters as shown in Fig. 2(a). First, a 100 nm thick SiO_2 layer was sandwiched

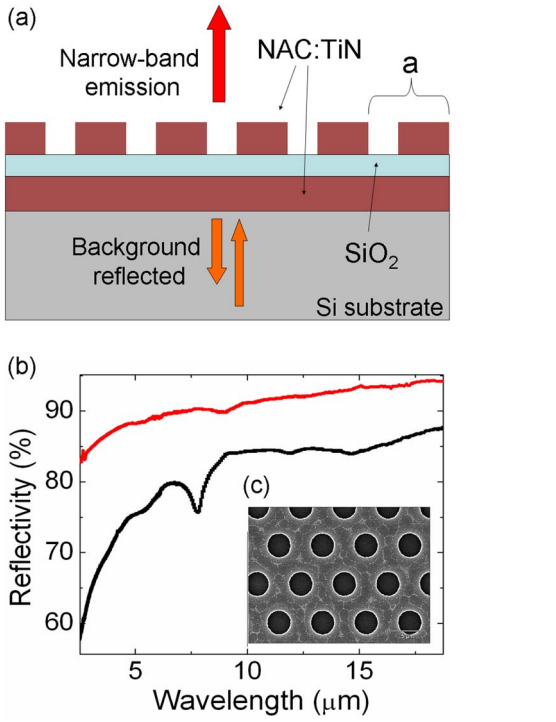

FIG. 2. (Color online) (a) IR emitter device fabricated using TiN doped NAC. The top film is patterned with a hexagonal lattice of air holes, and the bottom film serves as a reflector to suppress forward emitted background radiation from the substrate. (b) Reflectivities of the device (black squares) shown in (a) and an unpatterned device (red circles) with the same three-layer coatings. (c) A SEM top view of the micropatterned device is shown.

between two 200 nm thick TiN:NAC layers. The top NAC film was patterned with a hexagonal array of micron sized holes using Cl_2 plasma [Fig. 2(c)]. When heated, the patterned conducting film supports surface plasmon polaritons and emits narrow-band thermal radiation with a peak wavelength given with the following formula:

$$\lambda = a\left[\frac{4}{3}(i^2 + ij + j^2)\right]^{-1/2}\left(\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1 + \varepsilon_2}\right)^{1/2}. \quad (1)$$

Here, λ is the peak wavelength of emission, a is the lattice period, i and j are indices giving the order of the plasmon, and ε_1 and ε_2 are the dielectric permittivities of the two materials forming the interface, in this case the air/TiN:NAC or TiN:NAC/SiO_2. The bottom TiN:NAC film serves as a mirror that blocks the background radiation, and the SiO_2 film serves as a source for thermal radiation. As expected, the reflection spectrum of the patterned film shows a dip at the wavelength given by Eq. (1), which indicates increased absorption at this wavelength due to the surface plasmon mode [Fig. 2(b)].

The thermal emission spectrum of the NAC-based devices can be controlled by changing the lattice spacing, as shown in Fig. 3(a). Here, the devices were placed on a miniature hot plate, and their emission spectrum was collected at thermal equilibrium using an FTIR equipped with an external emission port. For the samples that were periodically patterned, the thermal emission is contained within a narrow bandwidth from $\Delta\lambda$=0.5 to 1.5 μm. The difference in bandwidths is attributed to the effects of fabrication imperfections: the roughness in the etch profile results in a broader spectrum. In contrast, the emission spectrum for a sample with identical coatings, but without the periodic lattice of

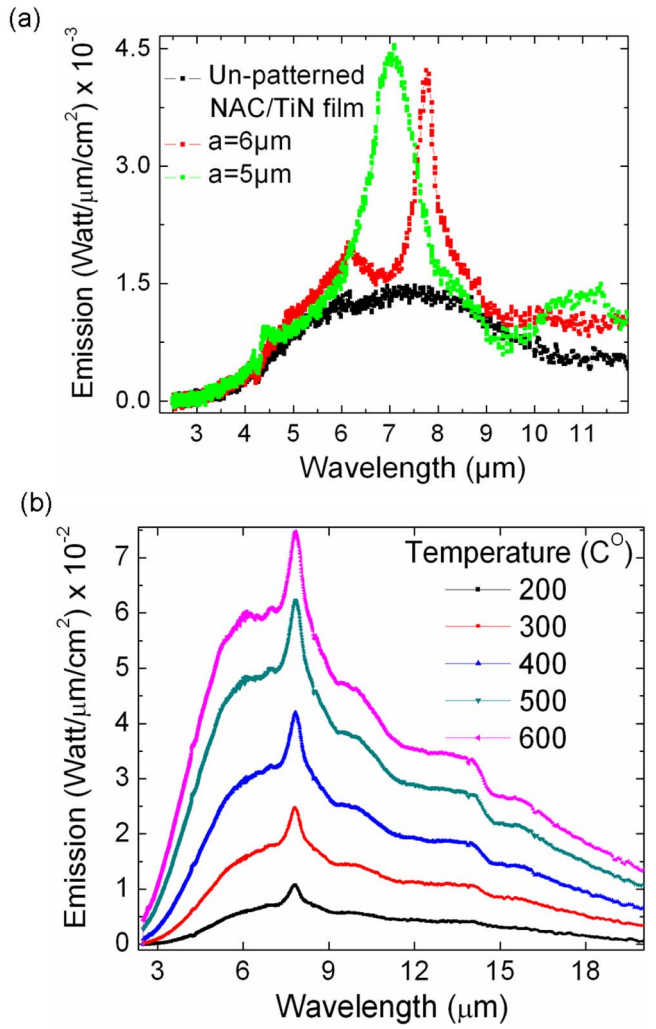

FIG. 3. (Color online) (a) Emission spectra of two devices patterned with different periodicities when heated to 150 °C, showing well-pronounced plasmonic peaks at the design wavelengths (red, green). Also shown is the emission from the device with no holes at the same temperature (black). (b) The emitted spectrum vs temperature for a device with $a=6$ μm.

holes, is the typical gray-body spectrum with a very broad bandwidth and no pronounced plasmonic emission peak. The micropatterned devices have in-band emissivities well exceeding that of the nonpatterned gray-body. In short, the plasmonic coupling results in both spectral narrowing and an increase in the in-band (useful) emitted radiation at the desired wavelength. Such a thermal emitter can be very useful as the emission spectrum can be set to a desired wavelength, and unlike black-body radiation the plasmonic peak of emission does not shift in wavelength with the changing temperature [Fig. 3(b)]. The devices are stable at temperatures of up to at least 600 °C (which is the limit of our measurement capabilities) for hours of operation in air without any protective coatings.

In conclusion, we have developed amorphous carbon films with favorable properties such as tunable conductivity and optical reflectivity for use in optoelectronic and MEMS applications. These films possess all of the superior properties of DL films, and in most cases exceed them, in areas such as resistance to electrical and thermal damage, extreme hardness, and surface smoothness. We have used plasma-based etching methods for micropatterning these materials and developed PTEs with carbon based materials. These devices emit narrow-band thermal radiation ($\Delta\lambda - 0.1\lambda$) in the mid-IR range when heated, and their emission spectra can be tuned to the desired wavelength by changing the microfabrication parameters. The NAC-based emitters can be operated up to 600 °C (and possibly more) in air without any degradation in their performance. The emission or reflection performance of these devices can be improved by optimizing the doping conditions or by modifying the device design. The development of thermal emitters based on amorphous DL films may have significant uses in areas where compact, efficient, and disposable mid-IR light sources are required such as sensing, military and environmental imaging, and spectroscopy of biochemical agents.

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