https://doi.org/10.1016/j.optcom.2016.07.053

Enhanced THz-to-IR emission from gas-surrounded metallic nanostructures by femtosecond laser irradiation

Liangliang Zhang,[1,2,3,a)] Tong Wu,[3] Hang Zhao,[3] Cunlin Zhang,[3] Wei Jin,[1] and X.-C. Zhang[4]

[1]*Department of Electrical Engineering and Photonics Research Center, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China*

[2]*Department of Optical Engineering, Beijing Institute of Technology, Beijing 100081, China*

[3]*Beijing Key Lab for Terahertz Spectroscopy and Imaging, Key Laboratory of Terahertz Optoelectronics, Ministry of Education, Department of Physics, Capital Normal University, No. 105 XiSanHuan BeiLu, Beijing 100048, China*

[4]*The Institute of Optics, University of Rochester, Rochester, New York 14627, USA*

Abstract: Enhanced terahertz-to-infrared (THz-to-IR) emission from gas-surrounded nanostructured metal films as a result of femtosecond laser irradiation is systematically investigated using selected gases. The dependencies of the THz-to-IR power on the gas species, gas pressure, and pump optical power are studied for Ar, N_2, Ne, and He. The experimental results reveal that the power of the THz-to-IR emission is related to the thermal conductivity of the gas in question. Moreover, the THz-to-IR emission power is dramatically enhanced when the gas pressure is close to zero.

***PACS**: 68.60.Dv; 73.20.Mf; 82.45.Yz*

Keywords: thermal effect; surface plasmons; nanostructured materials

[a)] Author to whom correspondence should be addressed. Electronic mail: zhlliang@126.com

Femtosecond laser-matter interactions have attracted broad interests in both theoretical and applied research.[1-3] It has been observed that a significant amount of residual thermal energy is deposited in metals following multi-shot femtosecond laser irradiation.[4-6] The remaining energy causes the bulk sample's temperature to rise. The temperature could be measured using an IR thermal camera. The surface temperature is proportional to $T_s \propto \frac{A\sqrt{a}}{k_m}$ when a bulk metal reaches thermal equilibrium, where A is the absorptivity of the incident laser, a is the thermal diffusivity, and k_m is the thermal conductivity of the metal.[7-9] The laser-induced surface temperature was sensitive to the intensity of the incident laser beam. Therefore, the measured surface temperatures followed a Gaussian distribution and the maximum peak temperature for Ru metal reached 750 K.[7] At this stage, the heated sample acts as a thermal radiation source. More recently, we identified intense terahertz-to-infrared (THz-to-IR) thermal radiation with a frequency spanning from the GHz range to several hundred THz from random metallic surface nanostructures that were smaller than the wavelength of the incident femtosecond laser.[7-9]

Ambient gas plasma produced near the metal surface has been shown to play a key role in the enhanced residual energy coupling.[10] In the presence of a metal surface, the threshold of gas ionization in front of the metal surface can be significantly reduced owing to the following factors: (1) gas exposed to the additional laser light reflected from the metal surface besides the incident light, and (2) energetic electrons escaping from the metal surface because of multi-photon photoelectron and thermionic emission.[11,12] A significantly enhanced residual energy has been observed following single-pulse ablation for various gases.[5,6] In our previous study, the surface roughness of our nanostructured metal films diffuses the surface backscattering, enhances the amount of reflected light absorbed by the air plasma, and subsequently enhances the gas-plasma-assisted heating of the sample.[9]

In this letter, we perform a systematic study of THz-to-IR emission from gas-surrounded metallic nanostructures as a result of femtosecond laser irradiation.

Among the four selected gases, Ar leads to the most intense THz-to-IR radiation. Moreover, the THz-to-IR emission power is dramatically enhanced when the gas pressure is close to zero, and remains almost unchangeable at higher gas pressures within our experimental range. Furthermore, we find that the power of the THz-to-IR emission increases as the thermal conductivity of the ambient gas decreases.

The sample substrate was a 60 μm thick anodic-aluminum-oxide (AAO) membrane with a pore diameter of 200 nm (Whatman, Germany). The pore density was approximately 50%. The metal was deposited on the membrane by magnetron sputtering using a JGP600 high-vacuum system with a base pressure of 1.5×10^{-5} Pa. The deposition rate was 0.5 nm/s, and the working pressure was 0.3 Pa. The metallic thin films had a nominal thickness of 100 nm and exhibited a random nanoscale surface roughness that was due to the through-pore structure of the AAO membranes. Three different types of metal – Ru, Pt, and Au – were used in the experiments. Figure 1 shows scanning electron microscopy (SEM) images of the top view (Fig. 1(a)) and the cross-sectional view (Fig. 1(b)) of the 100 nm thick Ru metal film; the Au and Pt samples also had thicknesses of 100 nm. The surface topography was similar for all of the tested metal films. The representative images show a variety of surface structures on the metal film, including voids and nanoprotrusions. It has been demonstrated that a stronger localized surface plasmon electric field (and, therefore, a more efficient thermal radiation source) exists at the metal/AAO interface.[8]

Figure 1(c) shows an illustration of the gas cell used in our experiment, the body of which was made of stainless steel. The entrance and exit windows were made of 2 mm thick fused quartz and 3 mm thick Si wafer, respectively, with diameters of 25 mm. The bottom of the cell was connected to a gas distribution system, which was able to pump the cell to a vacuum (i.e., below 3 Pa) or introduce a certain amount of each gas into the cell. The pressure inside could be precisely monitored with a pressure gauge. The experiment was performed with a Ti:sapphire regeneratively amplified laser system, which delivered 800 nm, 100 fs, 700 mW pulses at a 1 kHz repetition rate. The metallic nanostructured sample was placed in the beam path with

the metal surface facing the incident beam. The THz-to-IR emission was collected from the side of the sample that faced away from the beam, and was detected using a Golay cell detector that was equipped with a 6 mm diameter diamond input window (Microtech SN:220712-D). The detector exhibited a nearly flat response over a broad spectral range (i.e., 0.1–150 THz).

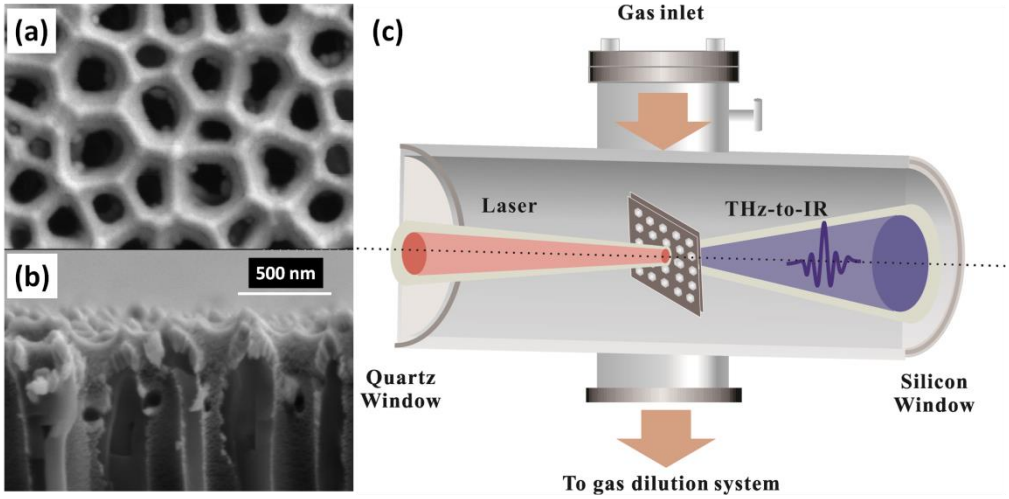

Figure 1. Panes (a) and (b) show scanning electron microscopy (SEM) images of the 100 nm thick Ru metal film. (a) Top view of the metal surface. (b) Cross-sectional view of the metal surface. The darkest regions indicate the absence of metal. (c) Schematic diagram of the gas cell used in our experiment.

Figure 2(a) shows the measured power of the THz-to-IR radiation from the 100 nm thick Ru sample surrounded by various inert gases – including He, Ne, N_2, and Ar – as a function of the gas pressure. As can be seen in Fig. 2(a), the radiation power varies for the four selected gases. Ar exhibits the highest radiation power; the power for N_2 and Ne fall in the middle; and the power for He is the lowest. Similar experimental results are also obtained using Au and Pt samples, which are shown in Figs. 2(b) and (c), respectively. This leads us to conclude that the enhanced THz-to-IR radiation is a general phenomenon that applies to the femtosecond laser irradiation of nanostructured metal films in a gas.

It is clearly observed that there is always a dip just before the gas pressure of 120000 Pa. We attribute the drop of measured power to the airflow in the chamber. When the gas pressure is from zero to standard atmospheric pressure (just before 120000 Pa), gas suction pump is used. And then, for obtaining pressure higher than 1*atm*, gas injection is used. Therefore, there is fluctuation of airflow at the pressure near

to 120000 Pa. The fluctuation could result in the drop of measured power. To eliminate the effects of THz-to-IR absorption by the ambient gas in the cell, we performed measurements of THz-to-IR radiation power from 1 mm thick ZnTe crystal in the selected gases at different gas pressures. We could not find any obvious variation of the radiation power in different gases within the pressure range of our experiment (data not shown).

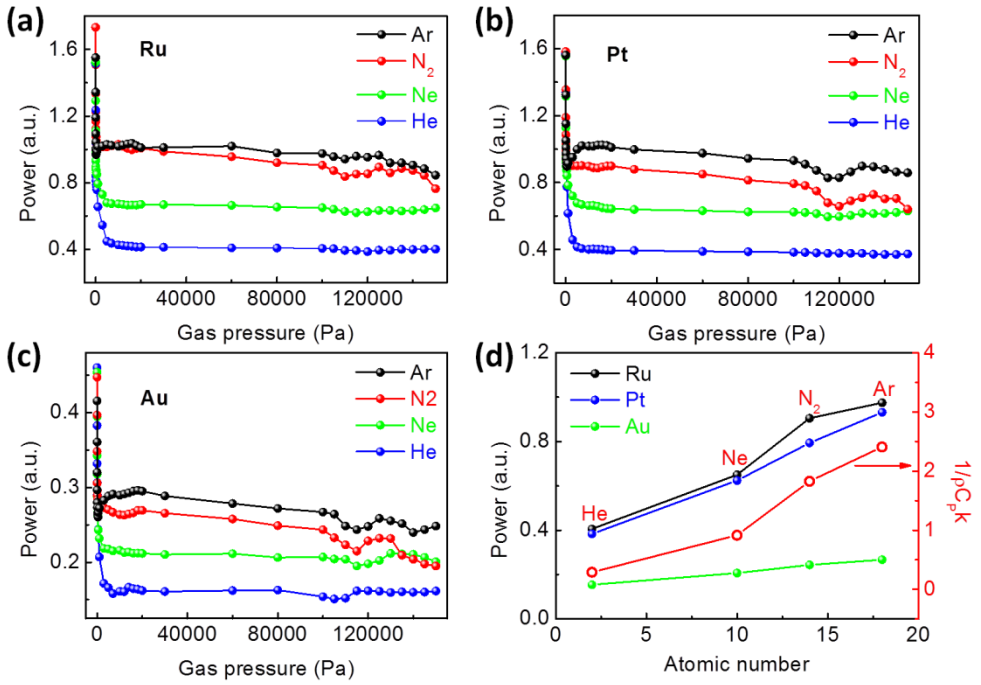

Figure 2. Panes (a–c) depict the measured terahertz-to-infrared (THz-to-IR) power from 100 nm thick nanostructured (a) Ru, (b) Pt, and (c) Au metal films as a function of the gas pressure for the four selected gases: He (blue), Ne (green), N_2 (red), and Ar (black). (d) Measured THz-to-IR power from Ru (black), Pt (blue), and Au (green) films at the gas pressure of 10^5 Pa versus the atomic number of the gas. The reciprocal values of the thermal conductivity (red) for different gases are also plotted.

For clarity, we plot the measured THz-to-IR radiation power at a gas pressure of 10^5 Pa versus the atomic number of the selected gases, as shown in Fig. 2(d). Based on the thermal radiation mechanism, the total power of THz-to-IR radiation from the nanostructured metal film is proportional to the fourth order of the surface temperature: $P \propto T_S^4$, where T_S is the surface temperature.[9] For a bulk metal surrounded by gas, the surface temperature is proportional to $T_S \propto \frac{A}{\sqrt{\rho C_P k}}$ when it reaches thermal

equilibrium, where A is the absorptivity of the incident laser, ρ is the gas density, C_P is the heat capacity, and k is the thermal conductivity of the ambient gas.[9,10] One factor that contributes to the THz-to-IR radiation enhancement is the increased absorptivity that is due to the ambient gas. For our nanostructured metal films, the surface roughness dramatically enhanced light absorption via an antireflection effect, which was caused by the gradient in the refractive index at an air/solid interface, and also via surface plasmon absorption.[13-16] The measured optical absorptivity was nearly 90% as a result of the structurally modifying surface.[8] As shown in Fig. 2(d), the output power of the THz-to-IR radiation from the Ru sample in Ar was twice as large as the value for He. This implies that, in addition to the direct absorption of the laser's energy, other mechanisms may play a key role in the gas-induced variation of THz-to-IR thermal radiation power.

Using the parameters associated with He, Ne, N_2, and Ar, we calculated the following values: $(\frac{1}{\sqrt{r C_p k}})_{He} = 0.82$, $(\frac{1}{\sqrt{r C_p k}})_{Ne} = 1.46$, $(\frac{1}{\sqrt{r C_p k}})_{N_2} = 1.74$, and $(\frac{1}{\sqrt{r C_p k}})_{Ar} = 2.48$.[17,18] We plot the values of $\frac{1}{\sqrt{r C_p k}}$ as a function of the atomic number in Fig. 2(d). Surprisingly, the shape of the radiation power curve (as a function of the atomic number) is consistent with the $\frac{1}{\sqrt{r C_p k}}$ value of the gas. Therefore, it is reasonable to suppose that the variation in THz-to-IR power in the different gases is caused by the difference in their thermal properties.

It is common that significantly enhanced THz-to-IR radiation is observed in all these gases when the gas pressure is close to zero. We attribute this effect to the change of the thermal conductivity of the gas, which may depend on the temperature and gas pressure. It is well known that k increases as the temperature increases, and decreases as the gas pressure decreases when the gas pressure is below 2670 Pa; furthermore, it remains constant when the gas pressure is between 2670 Pa and 196.2 MPa.[18] Moreover,

the gas density ρ decreases as the gas pressure decreases. Therefore, the surface temperature T_S is extremely high when the gas pressure is close to zero, and correspondingly the THz-to-IR radiation power is significantly enhanced.

To complete the characterization of THz-to-IR emission from nanostructured metal films in various gases under different pressures, we measured the dependence of the THz-to-IR power on the pump optical power by setting the gas pressure at three specific values: 10 Pa, 10^5 Pa, and 1.5×10^5 Pa. The surface temperature has been demonstrated that was proportional to the pump power.[9] Therefore, the THz-to-IR power is proportional to the pump power $P \propto P_{pump}{}^{n}$, where P_{pump} is the pump power and n is the exponent of the power law.

Figure 3 shows the results of the 100 nm thick Ru metal film surrounded by each of the four gases. The exponents of the power laws for the four selected gases at the gas pressure of 10 Pa were clearly consistent with each other, which are around ~1.65. We attributed the consistence to the identical thermal properties of all the gases when the gas pressure is close to zero. The results at the pressures 10^5 Pa and 1.5×10^5 Pa could be fitted using power laws with exponents of 1.53 (Ar), 1.48 (N_2), 1.36 (Ne), and 1.20 (He), respectively. The decrease in the exponents as the gas in question changes from Ar to N_2, to Ne, and then finally to He, which is closely influenced by the thermal conductivity of the ambient gas. The pump to THz-to-IR energy conversion efficiency increased with the pump fluence. It has been demonstrated that the maximum pump to THz-to-IR energy conversion efficiency for the Ru film reached 2.45%.[7] It is shown that the low gas pressure could enhance the conversion efficiency by ~50%.

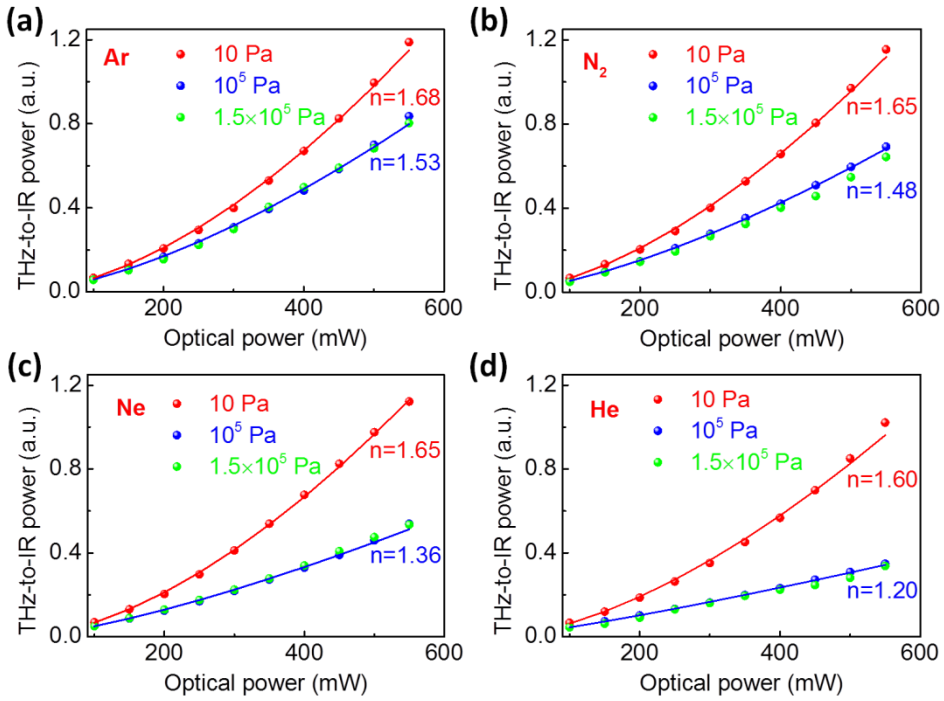

Figure 3. Terahertz-to-infrared (THz-to-IR) radiation power as a function of incident optical power at three specific gas pressures: 10 Pa (red), 10^5 Pa (blue) and 1.5×10^5 Pa (green) for the four selected gases: (a) Ar, (b) N_2, (c) Ne, and (d) He. The dots represent experimental data, whereas the lines represent calculated curves.

Energy transport from the plasma and heating by the shock wave traveling in the ambient gas along the sample surface may also contribute to the enhancement of the THz-to-IR radiation. More specifically, the formation of the gas plasma during a femtosecond pulse can enhance the thermal energy coupling to a sample according to the following two pathways: (1) the energy stored in the air plasma can be transferred to the sample; and (2) the re-deposition of the ablated material back onto the sample can be enhanced because of the high pressure of the ambient gas plasma, which remains long after the femtosecond laser pulse.[10]

The fact that the enhancement remains in experiments involving either a chemically inert gas or inactive material eliminates exothermic chemical processes as a major factor in enhancing the THz-to-IR emission; this is true despite the fact that chemical processes can occur between gases and chemically active materials at high temperatures. Our study therefore demonstrates that the thermal effects involved in femtosecond laser irradiation still constitute an interesting area that warrants further investigation.

To conclude, we demonstrated that the THz-to-IR emission from metallic nanostructures that results from femtosecond laser irradiation could be enhanced by surrounding the nanostructures with a gas that possesses a high thermal conductivity. Moreover, the emission can also be significantly enhanced by utilizing a low gas pressure. The thermal emission power monotonically increases with the atomic number of the gas for a given gas pressure. This property provides new guidelines for a broad range of THz-to-IR technological applications, such as a high-precision gas sensor.

Acknowledgements

The authors acknowledge support from the Hong Kong Scholars Program through project G-YZ53. This work was funded by the National Natural Science Foundation of China under grant No. 11374007 and the Foundation for the Author of National Excellent Doctoral Dissertation of PR China under grant No. 201237. It was also supported by the National Keystone Basic Research Program (973 Program) under grant No. 2014CB339806.

References

[1] D. F. Price, R. M. More, R. S. Walling, G. Guethlein, R. L. Shepherd, R. E. Stewart, and W. E. White, "Absorption of ultrashort laser pulses by solid targets heated rapidly to temperatures 1-1000 eV," Phys. Rev. Lett. **75**, 252 (1995).

[2] P. P. Pronko, S. K. Dutta, D. Du, and R. K. Singh, "Thermophysical effects in laser processing of materials with picosecond and femtosecond pulses," J. Appl. Phys. **78**, 6233 (1995).

[3] A. Y. Vorobyev and C. Guo, "Metallic light absorbers produced by femtosecond laser pulses," Adv. Mech. Eng., 1 (2010).

[4] A. Y. Vorobyev and C. Guo, "Direct observation of enhanced residual thermal energy coupling to solids in femtosecond laser ablation," Appl. Phys. Lett. **86**, 011916 (2005).

[5] A. Y. Vorobyev and C. Guo, “Enhanced absorptance of gold following multi-pulse femtosecond laser ablation,” Phys. Rev. B **72**, 195422 (2005).

[6] A. Y. Vorobyev and C. Guo, “Enhanced energy coupling in femtosecond laser-metal interactions at high intensities,’’ Opt. Express **14**, 13113 (2006).

[7] L. Zhang, K. Mu, J. Zhao, T. Wu, H. Wang, C. Zhang, and X.-C. Zhang, “Intense thermal terahertz-to-infrared emission from random metallic nanostructures under femtosecond laser irradiation,” Opt. Express **23**, 14211 (2015).

[8] L. Zhang, J. Zhao, T. Wu, H. Wang, C. Zhang, and X.-C. Zhang, “Terahertz-to-infrared emission through laser excitation of surface plasmons in metal films with porous nanostructures,” Opt. Express **23**, 17185 (2015).

[9] L. Zhang, K. Mu, Y. Zhou, H. Wang, C. Zhang, and X.-C. Zhang, "High-power THz to IR emission by femtosecond laser irradiation of femtosecond laser irradiation of random 2D metallic nanostructures," Sci. Rep. **5**, 12536 (2015).

[10] A. Y. Vorobyev, V. Kuzmichev, N. Kokody, P. Kohns, J. Dai, and C. Guo, "Residual thermal effects in Al following single ns- and fs-laser pulse ablation," Appl. Phys. A **82**, 357 (2006).

[11] S. Irvine and A. Elezzabi, “Pondermotive electron acceleration using surface plasmon waves excited with femtosecond laser pulses,” Appl. Phys. Lett. **86**, 264102 (2005).

[12] U. Kreibig and M. Vollmer, *Optical properties of metal clusters* (Springer, Berlin, 1995).

[13] J. Ready, *Effects of high-power laser radiation* (Academic Press, New York 1971).

[14] H. Raether, *Surface plasmons on smooth and rough surfaces and on gratings* (Springer, Berlin, 1988).

[15] I. R. Hooper and J. R. Sambles, “Coupled surface plasmon polaritons on thin metal slabs corrugated on both surfaces,” Phys. Rev. B **70**, 045421 (2004).

[16] E. N. Economou, “Surface plasmons in thin films,” Phys. Rev. **182**, 539 (1969).

[17] E. A. Mason and S. C. Saxena, "Approximate Formula for the Thermal Conductivity of Gas Mixtures," Phys. Fluids **1**, 361 (1958).

[18] J. Hilsenrath, C. W. Beckett, W. S. Benedict, L. Fano, H. J. Hoge, J. F. Masi, R. L. Nuttall, Y. S. Touloukian, H. W. Woolley, and C. V. King, *Tables of Thermal Properties of Gases* (National Bureau of Standards, Washington 1955).