

*Invited Paper***Nonlinear terahertz effects of gold nanofilms**Peidi Yang <sup>1</sup>, Baolong Zhang <sup>2,3</sup>, Jinglong Ma <sup>2</sup>, Yutong Li <sup>2,3</sup>, Jungang Miao <sup>1</sup>, and Xiaojun Wu <sup>1\*</sup><sup>1</sup> School of Electronic and Information Engineering, Beihang University, Beijing 100191, China<sup>2</sup> Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China<sup>3</sup> School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 100049, China\*<sup>1</sup> Email: xiaojunwu@buaa.edu.cn

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**Abstract:** Nonlinear interaction between strong-field terahertz electromagnetic waves and matters will become one of the next hot research frontiers in nonlinear optics. However, the lack of strong terahertz radiation sources and appropriate nonlinear terahertz materials have impeded its progress. Here we systematically have investigated the strong-field terahertz nonlinear effects of gold (Au) nanofilms on different substrates, including SiO<sub>2</sub>, high-resistivity Si and SiO<sub>2</sub>-high-resistivity Si hybrid substrates. The strong-field terahertz waves are emitted from lithium niobate crystals via tilted pulse front technique, and obvious nonlinear transmission responses are observed along with varying the incident field strengths for all the Au samples on the three types of the substrates. The nonlinear behavior is enhanced when the gold nanofilm thickness increases, which can be qualitatively understood by introducing the quantum tunneling effect and carrier multiplication theory generated at the Au nano-slits under the illumination of the strong-field terahertz pulses. Our demonstrations not only open a new paradigm for nonlinear terahertz investigations and future high-speed terahertz devices, but also provide an effective platform for exploring extreme terahertz sciences.

**Keywords:** Nonlinear terahertz effect, Gold nanofilm, Quantum tunneling, Carrier multiplication

**doi:**

**1. Introduction**

Nonlinear terahertz optics has become one of the most interesting research frontiers in nonlinear optics and futuristic technologies, fueling by its promising applications in 6G wireless communications, intelligent sensing, spectral imaging and so on [1]. To investigate this fascinating research field, powerful terahertz sources are significantly essential. In recent years, with the rapid development of ultrafast femtosecond laser technology and the popularity of strong terahertz pulse sources [2-5], it has been relatively easy to generate high-energy strong-field terahertz electromagnetic pulses in laboratory. It has been gradually reported that nonlinear terahertz effects can be realized by applying intense terahertz electromagnetic wave onto many materials [6-10], which makes the possibility of seeing the dawn of nonlinear terahertz optics.

These nonlinear terahertz materials include semiconductor materials, low-dimensional materials, metamaterials, nanomaterials and so on. Typical terahertz nonlinear effect like terahertz high harmonic generation (HHG) was first realized in GaSe through the optical difference frequency method in R.Huber's group in 2014 [7, 10]. Terahertz pulses were applied directly to GaSe crystals to radiate harmonic signals with frequencies covering up to  $675 THz$  [10]. In 2019, Hassan A. Hafez et al. employed the high repetition rate and strong terahertz pulses generated by electron accelerators in Dresden, Germany, to successfully excite terahertz HHG in graphene [7]. Subsequently, various strong-field terahertz induced low-dimensional materials have been used for studying HHG phenomena. However, this HHG phenomenon requires high repetition rates and peak electric fields of intense terahertz sources, which is extremely difficult for ordinary laboratories, solely equipped with conventional nonlinear crystals or two-color light induced air plasma terahertz sources. Therefore, the investigations of nonlinear terahertz phenomena conducted in ordinary laboratories is mainly achieved through field-induced collision ionization or tunneling effects with semiconductor materials [11, 12]. In addition, not only can the terahertz nonlinear effects be observed in pure semiconductors, but also phase changes can be induced by local field enhancement behaviors of metamaterials. [9].

Terahertz local field enhancement in metamaterials can excite substrate materials, which in turn can be employed for engineering the incident terahertz waves flexibly. This is the first stage of primitive nonlinear terahertz metamaterials [6]. In this way, it was observed that the metamaterial responses varied along with the incident terahertz field strengths. In some cases, the local field enhancement can even be applied to induce electroluminescence phenomenon in substrates [13]. Not only can metamaterials be employed to achieve terahertz field enhancement, but also terahertz electric fields can be directly coupled into metal nano-slits leading to nonlinear terahertz effects. For example, Kim et al. observed that terahertz waves can be effectively coupled into gold nano-slits resulting in a great field enhancement effect in 2009 [14]. In subsequent studies, they coupled intense terahertz fields into various gold nanomaterials and nanostructures, such as nanoparticles [15], nanocrystals [16], graphene composite gold nanocrystals [17], nano-opening metamaterials [18], triangular metal nanocrystals [19] to conduct systematic studies on nonlinear terahertz effects in gold. Recently, our group has demonstrated, for the first, large-scale nano-slit enabling terahertz metasurfaces on high resistivity silicon substrate, and successfully obtained field-induced frequency tunability and switching without extremely strong-field terahertz pulses [20]. The fundamental modulation mechanism was attributed to the strong-field induced impact ionization which is also a primary terahertz nonlinearity in semiconductors. However, when the strong terahertz electromagnetic waves irradiate into the metal nanostructure, electrons in the metal atoms may produce quantum tunneling current due to the field induced electron emission, resulting in a tunneling effect-enhanced nonlinear phenomenon plus the field-induced impact ionization. Most semiconductor devices are based on semiconductors or metals contacted semiconductors to form heterojunctions. When strong terahertz electromagnetic waves interact with such heterojunctions, both quantum tunneling effect and the field-induced impact ionization effect may contribute to the nonlinear behaviors. However, for composite substrates, the contribution weights of these two effects

have not yet been clearly unraveled.

In this work, we have demonstrated gigantic nonlinear terahertz effects in gold nanofilms fabricated on three substrates including  $\text{SiO}_2$ , high-resistivity Si, and their composite structures. The terahertz transmittance saturates along with the increase of the terahertz electric field strength. By comparing the influence of substrate type on nonlinear effect, we, for the first time, have disentangled the contribution weight of both quantum tunneling and carrier multiplication effect on nonlinear terahertz effect of gold nanofilm on  $\text{SiO}_2$ , high-resistivity Si, and their composite structures. It provides valuable references for further revealing nonlinear terahertz optical phenomena, accelerating the development of nonlinear terahertz devices.

## 2. Sample preparation and characterization

Ultrathin gold nanofilms with different average thicknesses were deposited on  $\text{SiO}_2$ , high-resistivity Si, and their composite structures. The thickness of the gold films is controlled by changing the fabrication time of gold atoms onto the substrates. All the films were prepared by sputtering and without any post-annealing. The surface morphology of the gold film was investigated by scanning electron microscopy (SEM), as shown in Figure 1 with different average thicknesses of  $d = 3, 4.5, 6,$  and  $9 \text{ nm}$ . It can be clearly seen from the figure that for ultrathin gold films, plenty of nano-gaps are naturally formed on the sample surface, which is very important for the subsequent strong-field terahertz-induced nonlinear responses.

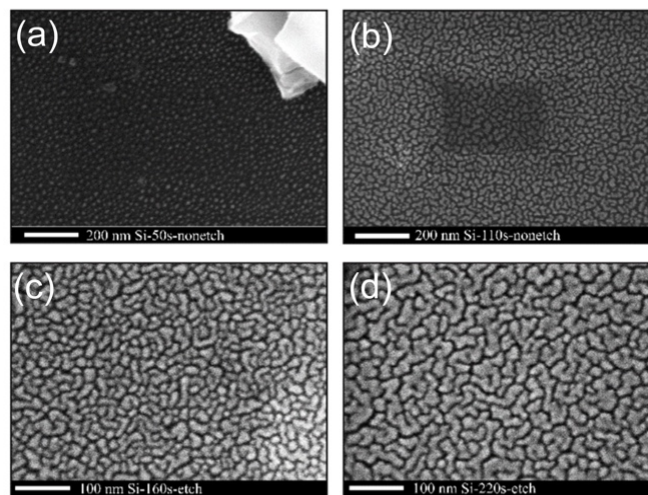


Fig. 1 SEM images of the gold nanofilms with average thicknesses of (a)  $3 \text{ nm}$ , (b)  $4.5 \text{ nm}$ , (c)  $6 \text{ nm}$ , and (d)  $9 \text{ nm}$ , sputtered on high-resistivity Si substrates.

To obtain a weak-field terahertz transmittance threshold, we first employ a terahertz time-domain spectrometer to characterize these samples. Figure 2(a)-(c) illustrate the terahertz temporal waveforms transmitted through the gold nanofilms with different thicknesses and the pure substrates. We define the terahertz transmittance as  $T = T_{out}/T_{in}$ , where  $T_{in}$  is the incident control signal without samples, while  $T_{out}$  denotes the transmitted sample signals. For the temporal waveforms as plotted in Figure 2(a)-(c), the terahertz transmittance continues to decrease with the increase of the gold film thickness. When we further summarize the terahertz peak signals, as exhibited in Figure 2(d)-(f), it is very obvious that the terahertz transmittance reduces along with the increase of film thicknesses. It indicates that the transmittance of weak-field terahertz electromagnetic waves is very high in the case of gold nanofilm thickness  $< 6 \text{ nm}$  due to the discontinuous film formation on the substrate surfaces. However, beyond this thickness, the terahertz reflection effect is enhanced and the transmittance reduces accordingly because of the good formation of the gold films.

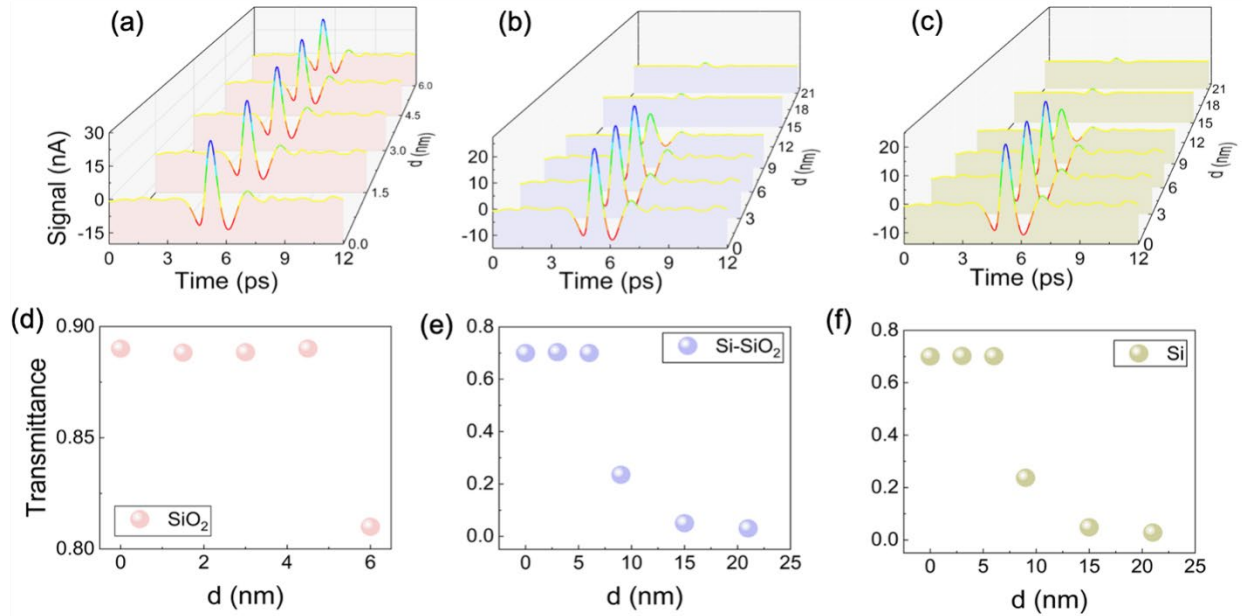


Fig. 2 Gold nanofilm thickness dependent terahertz waveforms for three substrates of (a)  $\text{SiO}_2$ , (b)  $\text{SiO-Si}$ , and (c)  $\text{Si}$ , and (d)-(f) their correspondingly summarized peak signals.

### 3. Strong-field terahertz nonlinear experiment

In the experiment of strong-field terahertz-induced nonlinear effects, we employ lithium niobate crystals to generate intense terahertz pulses via tilted pulse front technology [4, 21]. The terahertz source is pumped by a commercial Ti:sapphire femtosecond laser amplifier (Amplitude Technology company, center wavelength:  $800 \text{ nm}$ , pulse width:  $30 \text{ fs}$ , repetition frequency:  $10 \text{ Hz}$ ). For these measurements, the maximum terahertz single pulse energy is  $\sim 50 \mu\text{J}$ , and the corresponding peak

field can be estimated from the formula:  $W = \frac{\tau A |E_{THz}^{pk}|}{2\eta_0}$ , where  $W$  is the terahertz pulse energy,

$\tau$  presents the pulse width,  $A$  denotes the terahertz spot area at the focus,  $E_{THz}^{pk}$  is the peak value of the electric field, and  $\eta_0$  is the impedance of free space. We use a pair of terahertz polarizers (Tydex) to tune its intensity. A pyroelectric detector (Gentec, SDX-1152) is utilized to directly measure the transmitted terahertz single pulse energy, and a commercial terahertz camera (Ophire Company, Spiricon IV) is employed to image the focused terahertz beam profile. The peak calculated terahertz peak field is  $\sim 100$  kV/cm.

To further intuitively observe the nonlinear phenomenon, in the strong-field terahertz pumping case, we also define a terahertz transmittance coefficient, written as  $T_D = (T_1 - T_0)/T_0$ , where  $T_1$  and  $T_0$  are respectively the given terahertz electric field and the initial electric field. Firstly, we record the nonlinear effects happened on gold nanofilms fabricated on SiO<sub>2</sub> substrates. Figure 3(a) depicts the  $T_D$  variation trend for different gold film thicknesses on the SiO<sub>2</sub> with the increasing of the terahertz electric fields. The transmission coefficient exhibits the largest when the thickness of the gold film is 3 nm, and decreases as the film thickness increases, which is consistent with that observed in weak-field terahertz measurements. When the thickness of the gold film is 3 nm, the transmission coefficient is  $\sim 80\%$ . When the thickness increases to 6 nm, 45% can transmit the sample. With the increase of the terahertz electric field, the terahertz transmittance first increases linearly, and then saturated at  $\sim 70$  kV/cm for gold films with different thicknesses. The possible mechanism may be attributed to the generation of quantum tunneling current due to the delocalized electrons in the gold, resulting in the increase of the sample effective conductivity. The movement of the delocalized electrons produces tunneling current, leading to improved conductivity of the substrates. Therefore, the transmitted terahertz signals are largely reduced. Since the nano-slit width is narrow, the electron acceleration in these slits should be very short. The gained electron energy cannot be very high, and therefore, the gold film will not be destroyed when the electrons collide with the gold nano-slits on the other side with a certain momentum, making the repeatability possible of this experiment.

To further compare the nonlinear effects on different substrates, we also measure the transmission coefficient of high resistance silicon substrate with oxide film as a function of field strength under the same experimental conditions, as shown in Figure 3(b). When the thickness of the gold film is 3 nm, the transmission coefficient is 70%. However, it is reduced to  $\sim 35\%$  when the thickness of the gold film is 6 nm. Actually, nonlinear terahertz transmission phenomenon can be detected when there is a pure high-resistance silicon substrate [22], implying that strong-field terahertz pulses can generate field-induced carriers in high-resistance silicon. Therefore, the nonlinear phenomena observed in the Au nanofilm on high-resistance silicon substrates with oxide film may not only be from the quantum tunneling effect of the gold nanoslits, but also be caused by the carriers generated in silicon substrate.

Figure 3(c) shows the terahertz transmission coefficient of the pure high resistance silicon samples. When the thickness of the gold film is 3 nm, the transmission coefficient is ~60%, and when the thickness of the gold film is 6 nm, the thickness of the gold film is reduced to ~30%. We find that with the increase of terahertz electric field, the transmission coefficient of gold film first increases and then saturates at ~80 kV/cm. The experimental results exhibit the terahertz field induced nonlinearity tendency is, to some extent, consistent with that of silicon with oxide film substrate.

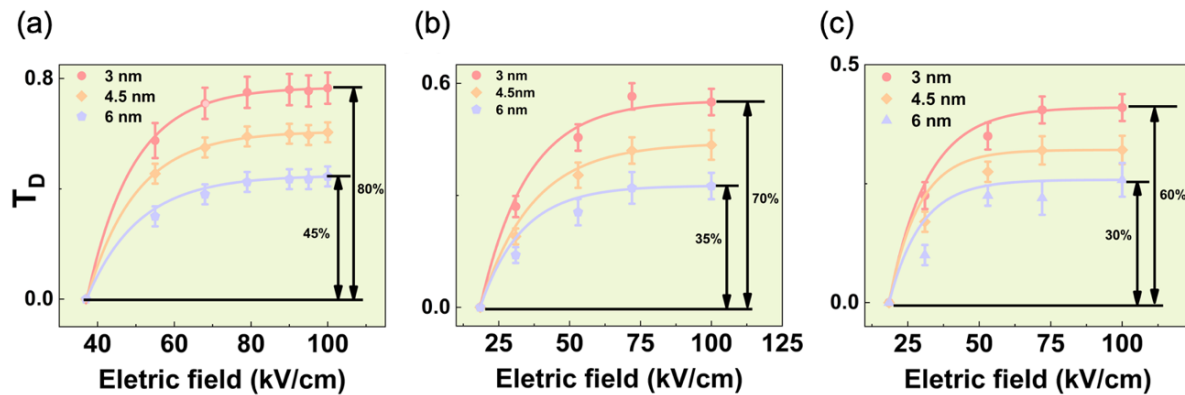


Fig. 3 Variation of terahertz transmission coefficient as a function of field strength for gold nanofilm samples on different substrates of (a) silicon dioxide substrate, (b) high resistance substrate with oxide film, and (c) high resistance silicon substrate.

To further directly compare the terahertz field-induced nonlinearity influenced by substrate types, we plot the 4.5-nm thick gold films on the aforementioned three substrates, as illustrated in Figure 4. The transmission coefficient of the substrate is normalized to exclude the influence of the transmission coefficient of the pure substrate materials on the nonlinear results. When considering the transmission coefficients for the three samples, we find that the high-resistance silicon substrate has the smallest transmission coefficient, while the silicon dioxide substrate gives the largest transmission coefficient. This manifests that the high-resistance silicon substrate has the strongest terahertz nonlinear modulation. Based on the previous experimental results, we have clarified that the nonlinear effect of the gold nanofilm on the high resistance silicon substrate induced by the strong terahertz field is mainly caused by the following three factors: (1) quantum tunneling of the nanogap on the gold film surface effect; (2) the carrier multiplication effect of the high resistance silicon substrate itself; (3) interaction between quantum tunneling and carrier multiplication effect.

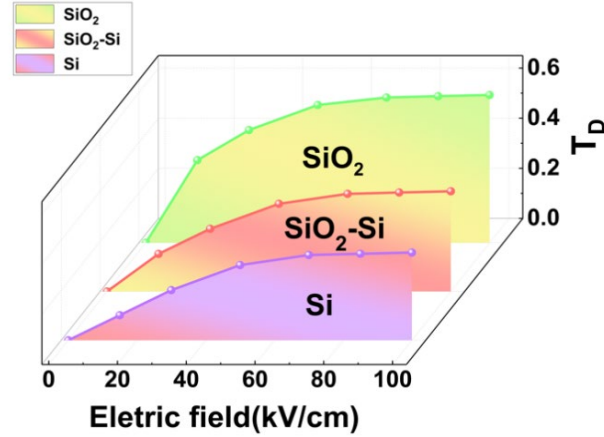


Fig. 4 Normalized terahertz transmission coefficients for three samples with different substrates. The fixed thickness of the gold nanofilm is 4.5 nm.

#### 4. Physical mechanism

Up to now, it has been clarified that the nonlinear terahertz effect mechanism observed on Au nanofilms can be qualitatively attributed to quantum tunneling and impact ionization and their interactions. To semi-quantitatively distinguish their contribution weight, we can first calculate the tunneling current at the nanoslits. According to the SEM images, we know that the average width of the nano gaps between the gold gaps is  $\sim 15$  nm. In the absence of an external electric field, the transmittance of electrons inside the gold atom through the barrier can be expressed as

$$T(L, E) = \frac{1}{\cosh^2(\beta L) + (\Upsilon/2)^2 \sinh^2(\beta L)} \quad (1)$$

where  $\left(\frac{\Upsilon}{2}\right)^2 = \frac{1}{4} \left( \frac{1-E/U_0}{E/U_0} + \frac{E/U_0}{1-E/U_0} - 2 \right)$ ,  $\beta = \sqrt{\frac{2m}{\hbar^2}(U_0 - E)}$ ,  $U_0$  is the height of the barrier. When an external electric field is applied, the effect of the terahertz electric field can be equivalently regarded as a decrease in the width of the barrier  $L$ , where  $L$  can be written as

$$L = \frac{U_0 - E}{e |E_{THz}|} \quad (2)$$

where  $E_{THz}$  is the magnitude of the external electric field. The tunneling current density at the nanogap is written as

$$I = nvT(L, E) \quad (3)$$

where  $n$  is the electron number density, and  $v$  is the average moving speed of electrons. Substituting the relevant parameters can obtain the tunneling current density at the gap due to the quantum tunneling effect which is about  $1.836 \times 10^{-4} A/cm^2$ .

In addition, we attribute the generation of a large number of carriers in high resistance silicon to the carrier multiplication effect induced by impact ionization. The movement of the electron in the electric field follows the dispersion law of the energy band structure in the momentum space, which can be described by the following equation

$$\hbar \frac{dk(t)}{dt} = -e \cdot \varepsilon(t) \quad (4)$$

where  $\hbar$  is the Planck constant,  $k(t)$  is the wave number,  $e$  denotes the electronic charge, and  $\varepsilon(t)$  is the terahertz field. Since the duration of incident terahertz waves can reach several picoseconds, the impact of phonon scattering on electrons cannot be ignored. Taking this into account, the equation of motion of electrons needs to add an attenuation term, so the equation of motion of electrons can be modified as

$$\hbar \frac{dk(t)}{dt} = -e \cdot \varepsilon(t) + \frac{k(t)}{\tau} \quad (5)$$

where  $\tau$  is the energy conversion time between photons and phonons. In our model, according to the nature of intrinsic silicon, we set the value of  $\tau$  is 1 ps. Only when the threshold kinetic energy of the valence band electrons  $E_{th}$  is higher than the band gap energy  $E_g$ , can the impact ionization process occur. Here,  $E_{th} = E_g \frac{2m_e + m_{hh}}{m_e + m_{hh}}$ , where  $m_e$  and  $m_{hh}$  are the effective masses of electrons and holes, respectively. When the above threshold energy is determined, the corresponding threshold wave number is also determined. The change of the electron wave number  $k(t)$  during the terahertz pulse is calculated based on the following assumption: when the electrons reach the average wave number  $\pm 2.51 \times 10^9 m^{-1}$ . That is, in infinite shock ionization, they will lose all their kinetic energy. When the wave number of the electron reaches this limit, an extra electron and a pair of e-h pairs will be produced, so the collision ionization will cascade, and the carrier density will increase to the second power.

By solving the above modified ordinary differential equation, the number of collisions can be obtained, and thus the total carrier density induced by collision ionization can be obtained. As drawn in the Figure 5, we substitute the initial parameters and simulate the corrected equation of motion, and finally obtain the curve of the electron wave number varying with time. At room



temperature, the band gap of high resistance silicon is  $1.14 \text{ eV}$ . Every time the electron wave number reaches the threshold wave number, twice of the carriers will be generated in the high resistance silicon. Figure 5(a) is the simulation result of high resistance silicon substrate with oxide film. The simulation results show that when terahertz wave is incident onto the high resistance silicon sample, 14 times of collision ionization occurs in the high resistance silicon, and  $2^{14}$  times as many carriers are produced. Such high carrier density increases the overall conductivity of the high resistivity silicon substrate, thus realizing the nonlinear effect of terahertz transmission. This also strongly supports our previous theoretical analysis.

In addition, for the samples with high resistance silicon substrate, the strong terahertz electric field will produce a huge field enhancement phenomenon in the nano gap, which will affect the carrier multiplication effect in the high resistance silicon substrate, and further improve the equivalent conductivity of the substrate. Therefore, the terahertz transmittance will be further reduced. By calculating the field enhancement at the gap and substituting the applied electric field and parameters, the above equation of electron motion is simulated. Figure 5(b) show that when the terahertz wave is incident onto the sample, 17 collisional ionization times can occur, so the collisional ionization of 2 times (more than 5 times) can be achieved. Compared with the previous single collision ionization effect, the field enhancement effect on the high resistance silicon substrate increases the carriers by an order of magnitude.

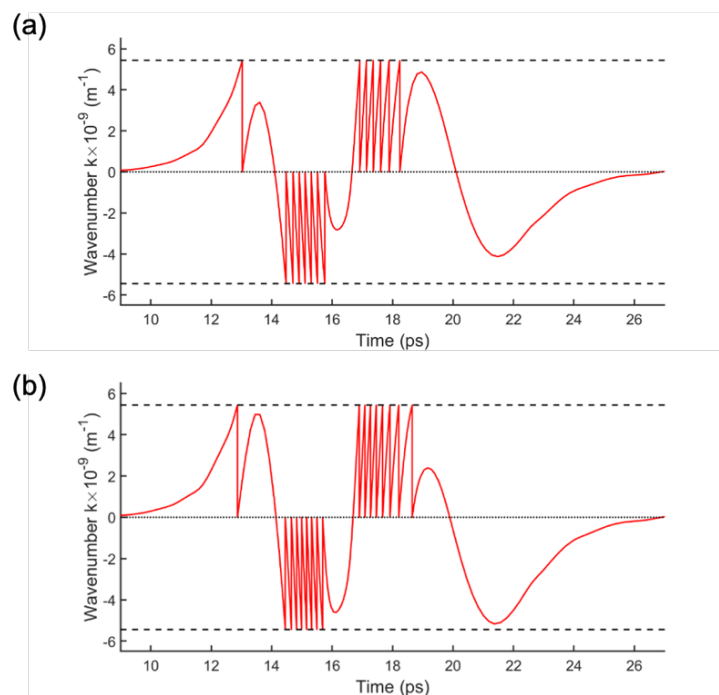


Fig. 5 Variation of electron wave number with time during collision ionization. (a) High resistance substrate with oxide film; (b) High resistance silicon substrate.

## 5. Conclusions

Through preparing gold nanofilms on silicon dioxide, high resistance silicon with oxide film and pure high resistance silicon substrates, the nonlinear phenomena and physical mechanism induced by intense terahertz electromagnetic pulse in gold nanofilms have been systematically investigated. The experimental results corroborate that the nonlinear effect of strong terahertz waves onto pure silicon substrates with Au nanostructures is more obvious than that of the other two substrates. This is mainly due to the interaction of quantum tunneling effect and carrier multiplication. At the same time, we have calculated the quantum tunneling effect in gold film and the carrier multiplication effect in high resistance silicon. Our next research work will focus on the physical simulation of this nonlinear effect, and extend this nonlinear effect to other new materials and new structures.

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