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Fast and sensitive lateral photovoltaic effects in Fe_3O_4/Si Schottky junction

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In this paper, we report the fast and sensitive lateral photovoltacic (LPE) effects in Fe_3O_4/Si junction. A good rectifying *I-V* characteristics and large LPE are observed in Fe_3O_4/Si junction. The LPE exhibits a linear dependence on the position of laser spot, and the position sensitivity can reach 32.5 mV mm^{-1}. The optical response time and relaxation time of LPE were ~60 ns and 5 μs, respectively. The enhanced LPE properties and the fast relaxation time in Fe_3O_4/Si junction were caused by the formation of the inversion layer in the interface of Fe_3O_4/Si.

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1. Introduction

Intensive research on the photovoltaic properties of semiconductors has been pursued for a long time due to their practical and wide application in optoelectronic devices. Both vertical and lateral photovoltaic effects have been observed in Schottky junction based on silicon with low cost, large photo-response and compatibility with the technology. The lateral photovoltaic effect (LPE) originates from the lateral diffuse flow and recombination of the photo-generated electron-hole pairs away from the laser spot.[1, 2] Since the LPE was first discovered by Wallmark in floating Ge *p-n* junction, this effect has been observed in many different systems.[1-6] The LPE output changes linearly with laser spot position and thus the LPE effect can be used in position–sensitive detectors (PSD) which can detect very small displacement. The response time and relaxation time of LPE are important characters for PSD applications. Because the LPE originates from the lateral diffuse transport of the excited carriers to the two electrodes from the laser spot, the photovoltage response time and relaxation time will be greatly influenced by the carrier mobility and resistance of the film. The Si-based devices of PSD had been used widely, and the response time of PSD was enhanced from milliseconds in amorphous silicon (a-Si) to microseconds in crystalline devices (c-Si), which due to the inherently slower carrier mobilities of a-Si compared with that of c-Si.[7] But the high resistance of silicon results in the slowly relaxation time of photovoltaic, which limited the practical purpose of PSD in the extreme conditions.[7, 8]

Interestingly, the LPE was observed in some simple metal-semiconductor (MS) structures.[9-11] The LPE in these MS shows large position sensitivities and good linearity, which is necessary for developing and designing high-sensitivity PSD. But the LPE is very sensitive to the metal thickness due to the shorting effect, so the metal thickness must be in nano-scale which will result in the instability and high resistance. Recently, Wang *et al.* have shown that the LPE of ferromagnetic metal film on Si substrate (FM/Si) can be tuned by the magnetic field, which suggested the LPE of FM/Si junction is strongly coupled to the magnetic alignment of the FM layer.[12] Furthermore, a large LPE of 97 mV mm^{-1} was observed in oxide-metal-semiconductor (TiO_2/Ti/Si) structure due to the increase of the surface resistivity. [13-15] These results suggest that large LPE can be achieved in Schottky junction with high resistivity films.

It is well-known that the oxide-film is stable in air and its' resistance is bigger than that of metal, so the oxide-film is a potential candidate for LPE in the PSD applications. But the LPE results in oxide-film/Si structure is still lacking.

In this paper, we report the fast and sensitive LPE effects in Fe_3O_4/Si junction. Large LPE and fast response/relaxation time are achieved. The inversion layer in the interface of Fe_3O_4/Si plays an important role to the photovoltaic properties. The parallel resistance of inversion layer and Fe_3O_4 film is higher than that of metal films and is lower than that of semiconductor, so a highest position sensitivity of 32.5 mV mm^{-1} and fast relaxation-time are achieved.

2. Experimental

The Fe_3O_4 thin films were prepared by pulsed laser deposition (PLD) on *n*-type Si (100) substrates with a 1.5 nm thick native SiO_2 layer on the surface. The target was α–Fe_2O_3. The films were prepared in a vacuum of 10^{-7} Torr at substrate temperature of 350 ℃ with different deposition time.[16] The pulsed excimer laser uses KrF (λ=248 nm) and produces a laser beam with an intensity of 1-2 J/$cm^2$and a repetition rate of 2 Hz. After the deposition, the film and substrate were annealed for 20 min. under the same condition.

The current-voltage ($I-V$) curve was measured with Keithley 2400 source and Keithley 2000 multimeter. The LPE was done using He-Ne laser (2 mW at 632 nm, made by Peking University) and Keithley 2000 multimeter. The time response of the LPE of Fe_3O_4/Si junction was measured using a Ti: Sapphire regeneration amplified laser system with a wavelength of 800 nm and 130 fs pulse duration and an oscilloscope of 100 MHz (Owon POS7102T).

3. Results and discussion

Figure 1 shows the x-ray diffraction pattern of 20 nm Fe_3O_4 film on Si with a native SiO_2 layer. Only diffraction lines of (111) family of Fe_3O_4 are observed, suggesting that a single-phase Fe_3O_4 film is formed and Fe_3O_4/Si junction is achieved.

Figure 2 (a) shows the dependence of resistivity of Fe_3O_4 film on temperature, which is measured on the surface of Fe_3O_4 film, as shown in the inset of Figure 2 (b). At low temperature, the resistance decreases with increasing temperature, which shows a typical behavior of thin Fe_3O_4 film, as the resistance data of Fe_3O_4 film on

MgO substrate in figure 2(a). When the temperature is increased beyond 230 K, the resistance drops rapidly because the conduction path starts to switch from the Fe_3O_4 film into the inversion layer underneath the native SiO_2 via thermally assisted tunneling.[16,17] The inversion layer can provide a low resistive path for carrier transport along the surface of the Si substrate, so the temperature dependence of resistivity shows remarkable current-controlled channel switching between Fe_3O_4 film and inversion layer in Fe_3O_4/Si structure, as shown in Figure 2(a). This result suggested that the measured resistivity at room temperature is the parallel resistance of inversion layer and Fe_3O_4 film in the Fe_3O_4/Si structure. Figure 2(b) shows the $I-V$ curve measured at 300 K in the plane of the Fe_3O_4 film. It is clear that the current increases nonlinearly with increasing voltage, which further confirms the existent of the inversion layer in the Fe_3O_4/Si junction.[16, 17]

Figure 3 shows the I-V curve of Fe_3O_4/Si junction with 20 nm Fe_3O_4 film at 300 K. Two indium electrodes with a 0.5 mm diameter were placed on the surface of Fe_3O_4 film and Si substrate, as shown in the inset of Figure 3. It is clear that the I-V curve exhibits a good backward diode-like rectifying character, which means the Fe_3O_4/Si structure is a Schottky junction. The junction current increases dramatically with increasing forward bias voltage. But the current remains very low for the reverse bias voltage even when the voltage reaches -4 V. Similar results had been observed by Qu *et al*. in Fe_3O_4/Si structure.[20] The work functions of Fe_3O_4 and Si are 5.3 and 4.4 eV, respectively.[18,19] Once the Fe_3O_4 thin film was deposited on the Si substrate, a large built-in field forms in the Fe_3O_4/Si and the Schottky junction is achieved,[20-23] which is good for the separation of electron-hole pairs in Si created by the radiation of the laser.

The LPE of the Fe_3O_4/Si junctions was investigated in detail. Two indium electrodes were placed on the surface of Fe_3O_4 film, as shown in the inset of Figure 4. The sample was always kept in the dark during measurements. When the Fe_3O_4 surface was partially illuminated by a He-Ne laser spot, a large LPE was found. The transmittance spectra of Fe_3O_4 films on MgO or Al_2O_3 substrates were shown in the inset of Figure 4. Obviously, there are slight absorbability of Fe_3O_4 from 400 to 800

nm, which is mainly due to its' thin thickness of Fe_3O_4 film. So a large absorption appears in Si substrates and the electron-hole pairs will be created in Si substrate under the radiation of the laser. Figure 4 shows the dependence of the induced photovoltage on the laser position for the Fe_3O_4/Si junction. The LPE shows an approximately linear dependence as the laser spot moves in the region between the two electrodes on the Fe_3O_4 surface and decreases when the laser spot moves out of the region, and the largest position sensitivity of 32.5 mV mm^{-1} in the linear region is achieved in 20 nm Fe_3O_4 film. Considering that the power of the laser illuminating the junction is only 2 mW and the contacts' distance is about 5 mm, the position sensitivity in Fe_3O_4/Si structure is very high. The position dependence of LPE can be well fitted using a traditional theory: $\mathrm{LPV} = K_0[\exp(-|L-x|/d) - \exp(-|L+x|/d)]$, where the K_0 is a proportional coefficient, L is the electrodes' position (as shown in Figure 4), d is the electron/hole diffusion length and x is the spot position.[10,24] The fitted data was shown in red line in Figure 4. This result clearly suggests that the LPE can be explained by the traditional theory. The LPE originates from the lateral diffuse flow and recombination of the created carriers away from the laser spot, and the large sensitivity value is due to the higher parallel resistance of inversion layer and Fe_3O_4 film. The photon energy of He-Ne laser is larger than the bandgap of Si, the electron-hole pairs will be created in Si substrate under the radiation of the laser. The laser spot is very small, and the electron-hole pairs can only be created at the illuminated region and separated by the built-in field. So the created holes will flow to the Fe_3O_4 film side, and then move away from the illuminated spot to the two electrodes on Fe_3O_4 film. The concentration of the created carriers is different at different distance from the illuminated spot, therefore, the lateral field is set up and the LPE is observed. It is well-known that the concentration of the created carriers will be greatly influenced by the resistivity— higher resistivity can suppress the diffusing of created carriers to the two electrodes and result in higher spatial variation of the LPE. The measured resistivity on the Fe_3O_4 surface in Fe_3O_4/Si structure is about 500 Ω at room temperature, which is higher than that of metal-based structure,

resulting in the created carriers hardly diffusing to the two electrodes compared to the Ti(Al)/Si structure.[13] This increases the difference in the concentration of the created carriers arriving at the two electrodes when the laser spot is not in the middle, so the enhanced LPE in Fe_3O_4/Si junction is achieved with ultrathin nano-crystalline Fe_3O_4 film.

The time response of the LPE of Fe_3O_4/Si junction was further investigated using a laser with a wavelength of 800 nm and 130 fs pulse duration and an oscilloscope of 100 MHz. Figure 5(a) shows the variation of the open-circuit LPE with time. The schematic circuit of the measurement is shown in the inset of Figure 5 (a). The rise time is about 3.8 μs and the full width at half maximum (FWHM) is about 72.5 μs when the LPE is directly measured. The FWHM stands for the relaxation time of LPE. The sharp rise time means that the LPE originates from the photo-induced voltage instead of thermoelectric effect.[25, 26] The input impedance of the oscilloscope is 1 MΩ which results in longer relaxation time due to the gradual decrease of LPE. To reduce the influence of the measurement circuit and simulate the true circuit, some resistances with different value were connected in parallel to the Fe_3O_4 film, as shown in the inset of Figure 5(b). Interestingly, ultrafast response and relaxation time of LPE was observed. The rise time dramatically reduces to about 60 ns and the FWHM is also reduced to about 5 μs, which means the optical response time and relaxation time of LPE were ~60 ns and 5 μs, respectively.

The vertical photovoltage effect (VPE) based on silicon has been widely used in solar cell and shows a picosecond response time which is much faster than the response time of LPE.[27, 28]The basic mechanism of both VPE and LPE is the separation of photo-generated electron-hole pairs spatially by the built-in field of the junction when the laser illuminates on the junction surface, but the origination of VPE and LPE is different. Once the laser illuminates on the junction, the created electron-hole pairs will be spatially separated by the built-in field and the VPE will be observed immediately, so an ultrafast photoelectric response is achieved. However, the LPE originates from the lateral diffuse flow and recombination of the created holes away from the laser spot after the electron-hole pairs was spatially separated by the built-in field, which will result in slower time response of LPE than that of VPE. But the response of LPE in Fe_3O_4/Si structure is much faster than that used in LPE devices, [13] and suggests good quality of Fe_3O_4/Si junction. The relaxation time of LPE

is greatly influenced by the measured resistivity between the two electrodes. The measured resistivity is the parallel resistance of inversion layer and Fe_3O_4 film in the Fe_3O_4/Si structure, which is higher than that of metal-based structure and is lower than that of semiconductor, so a fast response with microseconds relaxation time are achieved.

4. Conclusions

In conclusion, we have fabricated a Fe_3O_4/Si junction with good quality using PLD and investigated the LPE properties at room temperature. The rectifying behavior and large LPE were observed in the Fe_3O_4/Si Schottky junction. The dependence of the LPE on the position shows very highly sensitivity of 32.5 mV mm^{-1} as well as good linearity. The measured resistivity of Fe_3O_4/Si structure is higher than that of metal films, so a high position sensitivity and fast response with microseconds relaxation time are observed. The high position sensitivity and ultrafast response speed make the Fe_3O_4/Si junction promising for wide range of optoelectronic device applications.

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Notes and references

1 J. Wallmark, *Proc. IRE.*, 1957, **45**, 474.

2 B. F. Levine, R. H. Willens, C. G. Bethea and D. Brasen, *Appl. Phys. Lett.*, 1986,**49**, 1537.

3 R. H. Willens, *Appl. Phys. Lett.*, 1986, **49**, 663.

4 K. J. Jin, K. Zhao, H. B. Lu, L. Liao and G. Z. Yang, *Appl. Phys. Lett.*,2007, **91**, 081906 .

5 S. Q. Xiao, H. Wang, Z. C. Zhao, Y. Z. Gu, Y. X. Xia and Z. H. Wang, *Opt. Express*, 2008, **16**, 3798.

6 K. Zhao, K. J. Jin, H. B. Lu, Y. H. Huang, Q. L. Zhou, M. He, Z. H. Chen, Y. L. Zhou and G. Z. Yang, *Appl. Phys. Lett.*, 2006, **88**, 141914.

7 J. Henry and J. Livingstone, *IEEE Sensors J.*, 2006, **6**, 1557.

8 E. Chen and S.Y. Chou, *Appl. Phys. Lett.* , 1997, **70**, 753.

9 J. Henry and J. Livingstone, *Adv. Mater.* , 2001, **13**, 1022.

10 S. Q. Xiao, H. Wang, Z. C. Zhao and Y. X. Xia, *J. Phys. D: Appl. Phys.* , 2007, **40**, 5580.

11 S. Liu, H. Wang, Y. J. Yao, L. Chen, and Z. L. Wang, *Appl. Phys. Lett.*, 2014, **104**, 111110.

12 S.H. Wang , W.X. Wang , L.K. Zou , X. Zhang , J.W. Cai , Z.G. Sun ,B.G. Shen and J.R. Sun. *Adv. Mater.*, 2014, **26**, 8059.

13 L. Du and H. Wang, *Opt. Express*, 2010, **18**, 9113.

14 C. Q. Yu, H. Wang, S. Q. Xiao and Y. X. Xia, *Opt. Express*, 2009, **17**, 21712.

15 C. Q. Yu, H. Wang and Y. X. Xia, *Appl. Phys. Lett.* , 2009, **95**, 263506.

16 X. J. Wang, Y. Sui, J. K. Tang, C. Wang, Z. Lu, X. Q. Zhang, Z. G. Liu, W. H. Su, X. K. Wei and R. C. Yu, *Appl. Phys. Lett.* **,** 2008**, 92**, 012122.

17 J. K. Tang, J. B. Dai, K. Y. Wang, W. L. Zhou, N. Ruzycki and U. Diebold, *J. Appl. Phys.* , 2002, **91**, 8411.

18 M. Fonin, R. Pentcheva, Yu. S. Dedkov, M. Sperlich, D. V. Vyalikh, M. Scheffler, U. Rüdiger and G. Güntherodt, *Phys. Rev. B*, 2005, **72**, 104436 .

19 F. G. Allen and G. W. Gobeli, *Phys. Rev.*, 1962, **127**, 150.

20 T. L. Qu, Y. G. Zhao, H. F. Tian, C. M. Xiong, S. M. Guo and J. Q. Li, *Appl. Phys. Lett.* , 2007, **90**, 223514.

21 W. B. Mi, E. Y. Jiang, and H. L. Bai, *J. Appl. Phys.* , 2010, **107**, 103922.

22 Z. Viskadourakis, M. L. Parames, O. Conde, M. Zervos, and J. Giapintzakis, *Appl. Phys. Lett.* , 2012, **101**, 033505.

23 J. Panda, P. Banerjee and T. K. Nath, *J. Phys. D: Appl. Phys.* , 2014, **47**,415103.

24 L. M. Chi, P. F. Zhu, H. Wang, X. A. Huang and X. T. Li, *J. Opt.* , 2011, **13**, 015601.

25 P. X. Zhang, W. K. Lee and G. Y. Zhang, *Appl. Phys. Lett.*, 2002, **81**, 4026.

26 J. R. Sun, C. M. Xiong, B. G. Shen, P. Y. Wang and Y. X. Weng, *Appl. Phys. Lett.* , 2004, **84**, 2611.

27 H. B. Lu, K. J. Jin, Y. H. Huang, M. He, K. Zhao, B. L. Cheng, Z. H. Chen, Y. L. Zhou, S. Y.

Dai and G. Z. Yang, *Appl. Phys. Lett.* , 2005, **86**, 241915.

28 J. Xing, K. J. Jin, M. He, H. B. Lu, G. Z. Liu and G. Z. Yang, *J. Phys. D: Appl. Phys.* , 2008, **41**, 195103.

Figure captions

Figure 1 The XRD pattern of Fe_3O_4 film on Si.

Figure 2 (a)The variation of the resistivity of Fe_3O_4 with temperature; (b) the *I-V* curve of Fe_3O_4/Si structure at 300 K. the inset exhibits the schematic setup for measurement.

Figure 3 The *I-V* curve of Fe_3O_4/Si junction at 300 K, the inset shows the schematic circuit of the junction measurement;

Figure 4The dependence of the lateral photovoltage on the laser position for Fe_3O_4/Si junction, the inset exhibits the schematic setup for LPE measurement and the transmittance spectra of Fe_3O_4 films on MgO or Al_2O_3.

Figure 5 (a)The variation of the open-circuit LPE with time, the schematic circuit of the measurement is shown in the inset; (b) The variation of the LPE with time, a resistance was connected in parallel to the Fe_3O_4 film, the schematic circuit of the measurement is shown in the inset.

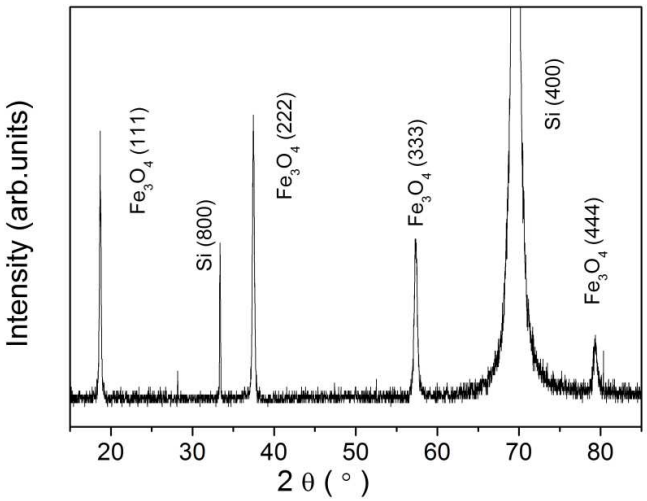

Figure 1

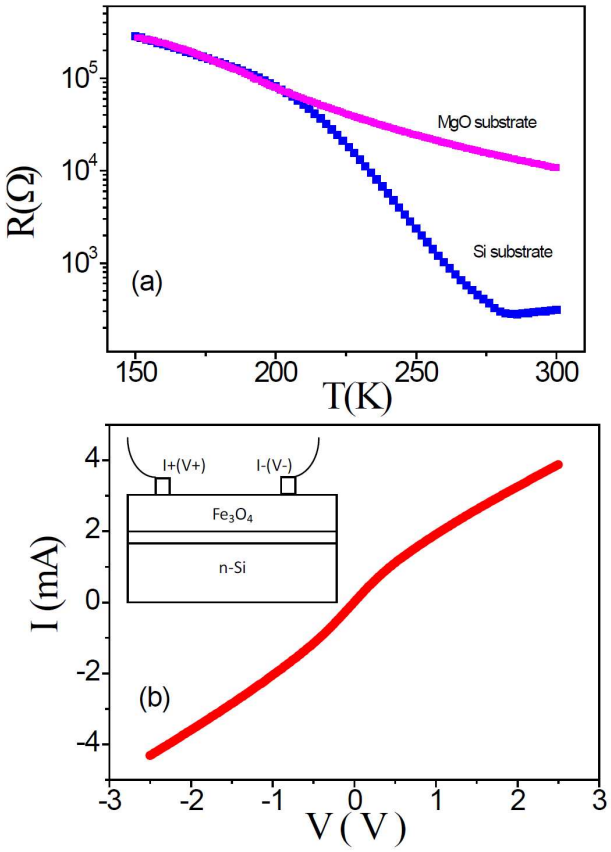

Figure 2

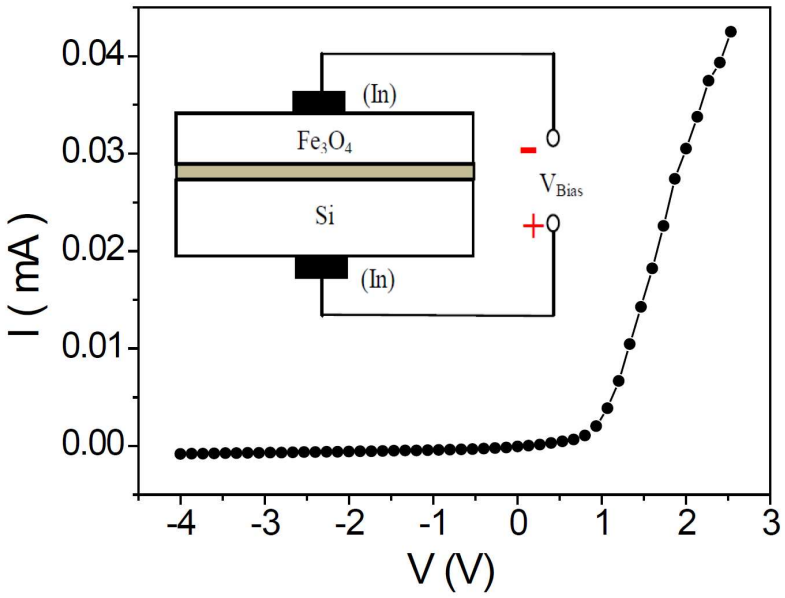

Figure 3

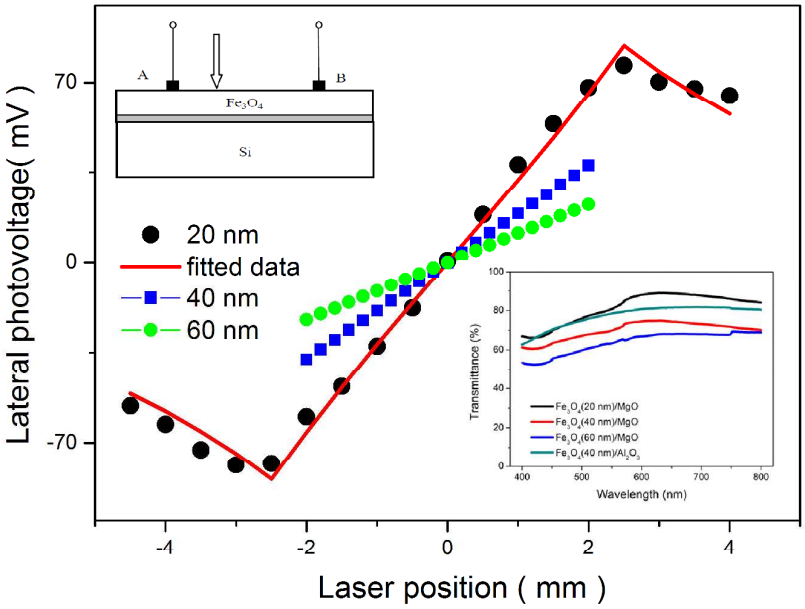

Figure 4

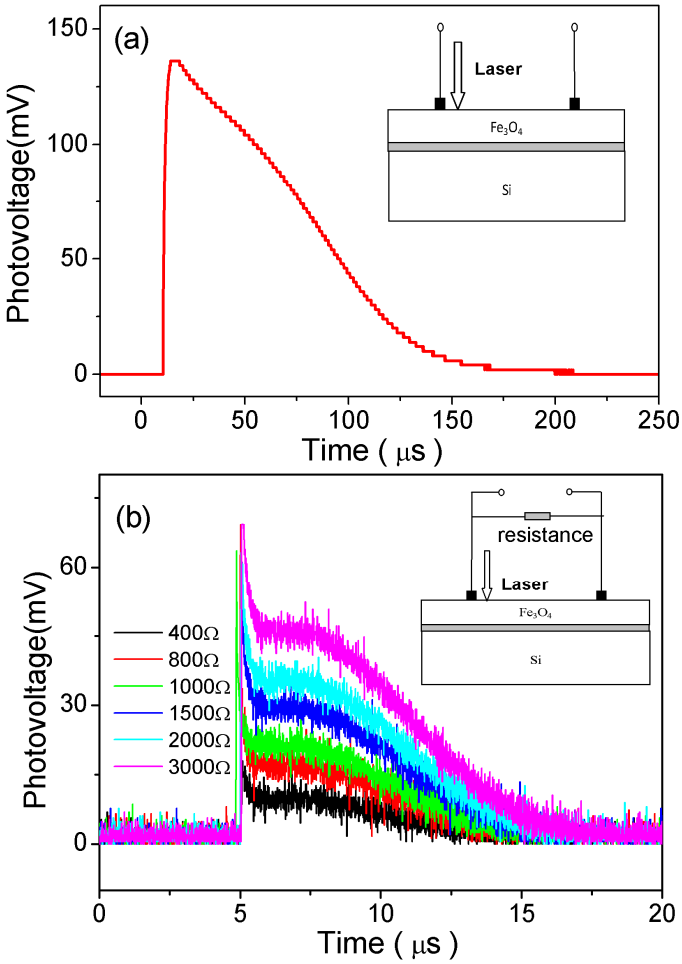

Figure 5