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Investigation of Terahertz Emission from BiVO$_4$/Au Thin Film Interface

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Abstract We demonstrate emission of terahertz pulses from a BiVO$_4$/Au thin film interface, illuminated with femtosecond laser pulses. Based on the experimental observations, we propose that the most likely cause of the THz emission is the Photo-Dember effect caused by the standing wave intensity distribution formed at the BiVO$_4$/Au interfaces.

1 Introduction

Terahertz (THz) pulses can be generated in non-linear optical crystals, metals, and semiconductors using ultrashort laser pulses that excite currents and polarizations [1, 2]. For example, THz radiation can be generated by illuminating thin semiconductor layers deposited on metal surfaces [3, 4]. When a femtosecond laser pulse

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is incident on such a semiconductor-metal junction, a transient current is formed in the Schottky depletion layer of the metal/semiconductor interface, which gives rise to the emission of an electromagnetic transient in the THz range. In the past, THz emission from, mostly, conventional semiconductors like gallium arsenide, silicon, germanium, and some unconventional ones, such as cuprous oxide, has been studied [5].

In general, there are two generation mechanisms which are important in the case of THz generation from semiconductor surfaces and interfaces. When a metal comes into contact with a semiconductor, the metal-semiconductor junction forms either a Schottky, or an ohmic contact depending on the barrier height. Due to the depletion field present near the Schottky barrier, the photoexcited carriers accelerate and form a photocurrent normal to the surface which gives rise to THz emission [6–9].

In the case of narrow-bandgap semiconductors, where the surface depletion field is weaker, we can have THz emission through the photo-Dember effect. In the photo-Dember effect, the incident light is absorbed near the surface of the semiconductor thin film. When the absorption is strong, more charge carriers are generated near the surface of the semiconductor compared to deeper into the material. As a result, a non-uniform carrier distribution is built up and a carrier gradient is formed. When, in addition, the mobilities of the electrons and holes are also different, they diffuse with different velocities. As a result, a transient dipole is rapidly formed near the surface. This time-dependent dipole, which is parallel to the concentration gradient and perpendicular to the excited surface, gives rise to THz radiation [10, 11]. THz emission from the photo-Dember effect has been reported for many different materials, like InAs, InN etc. [12–14]. In 2010, Klatt et al. showed THz emission from lateral photo-Dember currents by partially masking the semiconductor surface with a metal layer. When excited with femtosecond laser pulses, this gives rise to a laterally non-uniform carrier distribution, which emits THz radiation [15].

The study of THz pulses emitted from semiconductors and semiconductor/metal interfaces gives us information about the carrier dynamics and the carrier transport properties in the semiconductors. In cases when the THz generation mechanism is initially not known, careful examination of the properties of the emitted waveforms can help us discover the source of the emission.

Here, we present results on the emission of THz radiation, after illumination with femtosecond laser pulses of the material bismuth vanadate ($BiVO_4$), which is a promising material for solar water splitting and photocatalysis [16, 17]. We find that the emitted THz amplitude increases linearly with the incident pump power indicating a second-order nonlinear optical process as the source of the emission. We examine the topography of the deposited $BiVO_4$ thin films using atomic force microscopy (AFM) and investigate the optical properties using reflection spectroscopy. Samples with an insulating SiO_2 layer in between the $BiVO_4$ and the gold are found to emit THz signals comparable in strength to samples without such a layer. This indicates that built-in electric fields, associated with Schottky barrier formation, are less likely to be the source of the emission. Instead, we propose the longitudinal photo-Dember effect as the generation mechanism responsible for the THz emission.
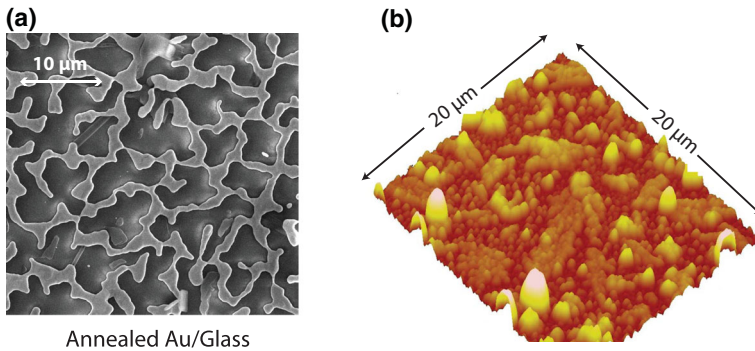
Fig. 1 **a** Scanning electron microscope (SEM) image of a 1000-nm-thick gold film after annealing at 450 °C for around 2 h. **b** AFM scan showing the topography of a 20 μm x 20 μm area of a 200-nm-thick BiVO$_4$ film deposited on the glass substrate

2 Experimental

2.1 Sample Preparation

For the sample, a 100-nm-thick gold film was deposited on the glass substrate using electron beam evaporation. For adhesion purposes, a 10-nm-thin chromium layer was deposited first. Then, different thicknesses (20–300 nm) of BiVO$_4$ were deposited on top of the gold film using a spray pyrolysis technique, which is discussed in detail elsewhere [18, 19]. Due to its high visible light absorption and high chemical stability, BiVO$_4$ acts as an efficient catalyst and splits water into hydrogen and oxygen upon illumination. Apart from showing high visible light photoactivity, it has many other interesting properties as well, such as ferroelasticity, photochromism and ionic conductivity [20, 21]. BiVO$_4$ prepared using the spray-pyrolysis method is reported to be monoclinic in nature and an n-type semiconductor [22, 23]. Among the three available crystal phases of BiVO$_4$, monoclinic BiVO$_4$ (m-BiVO$_4$) is an important material with many applications. It is a wide band semiconductor with a bandgap of 2.4 eV ($\approx$520 nm) and it exhibits much higher photocatalytic activity with respect to the other polymorphs [24–26]. The bandgap of BiVO$_4$ is around 520 nm (2.4 eV) hence ideally it should have little or no absorption at a wavelength of 800 nm (1.5 eV) pump light. However, when 800 nm wavelength pump light is incident on the BiVO$_4$ film at a 45° degree angle of incidence, a significant amount of absorption is observed presumably due to the impurities/defects introduced during the preparation. The amount of absorption is not exactly known, since some scattering of the light also occurs, which may give rise to an additional, *apparent* absorption.

During the deposition of BiVO$_4$, the sample (glass substrate coated with gold thin film) is heated at 450 °C for around 2 h. As a result of the heating, the surface of the bare gold becomes rough and discontinuous and there is a formation of big islands. In Fig. 1a, we show a scanning electron microscope (SEM) image of a 100-nm-thick gold film after heating at 450 °C for around 2 h. Heating of the sample while spraying leads to drying and crystallization of BiVO$_4$. In Fig. 1b, we show the topography of
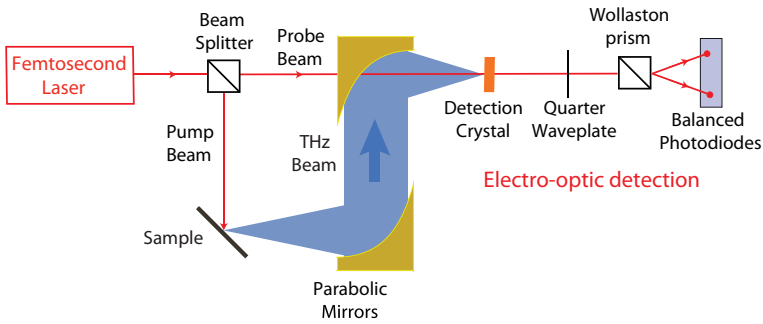
Fig. 2 Experimental setup for THz generation and detection

a 20 μm x 20 μm area of a 200-nm-thick BiVO₄ film, deposited directly on a bare glass substrate, as measured with an atomic force microscope. The surfaces of the prepared BiVO₄ thin films are quite rough. For a 200-nm-thick film, the root mean square (RMS) roughness was estimated to be around 20 nm.

2.2 THz Generation and Detection Setup

The experimental setup is schematically shown in Fig. 2. We use a Ti:Sapphire oscillator which has a center wavelength of 800 nm, pulse duration of 50 fs, average power of 800 mW and a repetition rate of 11 MHz. When ultrashort pulses from the laser oscillator are incident on the sample at a 45 ° angle of incidence, THz emission is observed. A pair of gold coated parabolic mirrors is used for collecting, collimating, and finally focusing the THz radiation onto a 500-μm-thick zinc telluride (ZnTe) (110) electro-optic detection crystal. The electric field of the THz radiation induces a small birefringence in the electro-optic crystal. At the same time, a part of the same ultrashort laser pulse that was used to generate the THz pulse is incident on the detection crystal.

When the linearly polarized probe beam propagates through the electro-optic crystal, due to the THz induced birefringence, it acquires a small elliptical polarization. Then, the probe beam passes through a Wollaston prism which separates the beam into two orthogonal components. A differential detector, consisting of two photodiodes, measures the difference in the intensities which is proportional to the instantaneous THz electric field. By varying the time-delay between the pump pulse and the probe pulse, the THz electric field is measured "stroboscopically" as a function of time.

3 Results and Discussion

In Fig. 3a, we show the measured THz electric field as a function of time, emitted from a 100-nm-thick BiVO₄ film deposited on a thick gold film with a 100 nm average thickness. The amplitude of the emitted THz electric field is roughly around 0.2 % of the THz emission from a conventional semi-insulating GaAs (100) surface

(a)

(b)
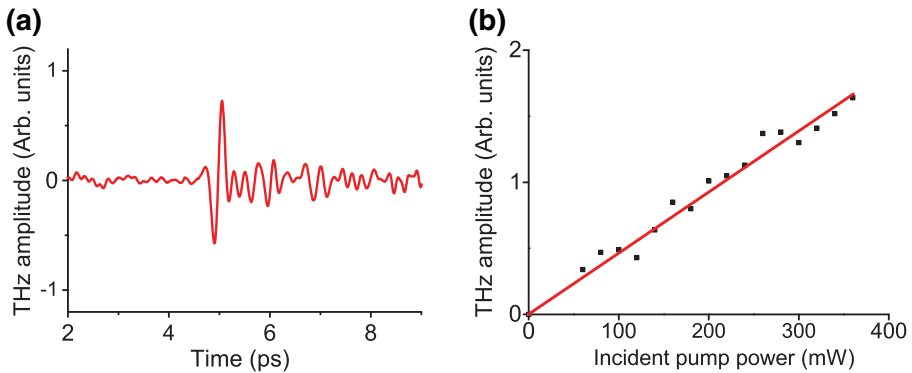
Fig. 3 **a** Measured THz electric field emitted from a 100-nm-thick $BiVO_4$ film deposited on a 100-nm-thick gold film, plotted vs. time. **b** Measured THz amplitude plotted as a function of the incident laser power

depletion field emitter and is comparable to the emission from percolated gold [27]. Tight focusing of the pump beam is avoided to prevent any damage to the sample. The emitted THz amplitude increases linearly with the laser power incident on the sample as shown in Fig. 3b. This suggests that a second order non-linear optical process is responsible for the THz emission. The $BiVO_4$ layer deposited using the spray pyrolysis method is not uniform. Combined with the large surface roughness, already shown in Fig. 1b, this makes it difficult to get an accurate estimate of the thickness of the $BiVO_4$ layer. This non-uniformity in the thickness gives rise to a variation in the THz amplitude. Hence, as we go from one spot to the other on the sample, there is a variation of around ± 10 percent of the peak to peak amplitude of the emitted THz radiation.

In the literature, $BiVO_4$ thin films deposited on the gold surface are reported to show a diode-like behavior, suggesting that the $BiVO_4$/Au junction forms a Schottky interface [28]. In Fig. 4a, we schematically show the energy band bending between gold and $BiVO_4$, which is an n-type semiconductor. In order to determine if the depletion field is responsible for the THz generation in our case, we included SiO_2 dielectric layers of varying thickness between the $BiVO_4$ layer and the gold layer. Due to the SiO_2 layer, the carrier transport between gold and $BiVO_4$ is strongly reduced, which should hinder the formation of a depletion field. However, during the deposition of $BiVO_4$, due to heating, there is a risk of destroying the ultrathin SiO_2 layer. In that case, the $BiVO_4$ film can again come into direct contact with the gold layer and form a Schottky junction. To check if the SiO_2 layer is still intact after heating for 2 h, we inspect the samples using the current-voltage (I–V) characteristics. In Fig. 4b, we show the I–V curves for the bare gold thin film and the gold thin film with 20 nm SiO_2 layer on top. We measure a significant current for the bare gold thin film but very little current is measured for the SiO_2/Au layers which confirms that even after heating, the SiO_2 layer is not getting destroyed and remains intact.

Moreover, the sample is also characterized using scanning electron microscopy (SEM). In Fig. 4c, we show the SEM image of the gold thin film coated with a
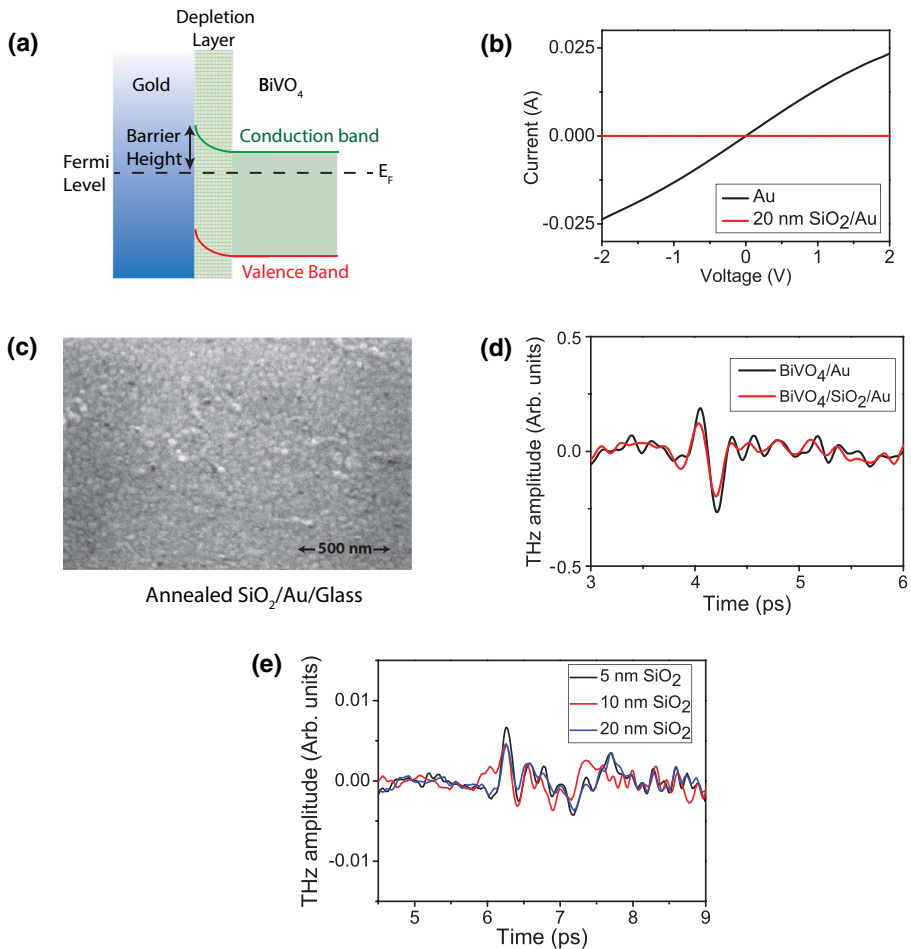
Fig. 4 **a** Schematic representation of the energy band bending between $BiVO_4$ and gold thin films **b** I–V characterization of a bare gold thin film and gold thin film with 20 nm SiO_2 deposited on top. No current is measured for the SiO_2/Au sample, which confirms that even after annealing, the silica layer is not destroyed. **c** SEM image of SiO_2/Au after annealing at 450 °C for around 2 h. **d** Comparison of THz emission from $BiVO_4$/Au and $BiVO_4$/5 nm SiO_2/Au. The emitted THz amplitudes are comparable even after the inclusion of SiO_2 layer. The thickness of the $BiVO_4$ film is 100 nm. **e** Measured THz electric field emitted from $BiVO_4$/SiO_2/Au samples for 5, 10, and 20 nm thick SiO_2 layers

20 nm SiO_2 layer, after heating at 450 °C for 2 h. Interestingly, it is observed that when a 20-nm-thin SiO_2 layer is present on top of gold, the surface of the annealed $BiVO_4$/Au sample is much smoother compared to the surface of the annealed bare gold film. This gives a clear indication that the SiO_2 layer sandwiched between the gold thin film and the $BiVO_4$ thin film remains intact even after heating. In Fig. 4d, we compare the amplitude of the THz radiation emitted from $BiVO_4$/Au and from $BiVO_4$/SiO_2/Au samples with a silica layer thickness of 5 nm. We observe that the THz amplitude remains largely unaffected after the inclusion of the thin SiO_2 layer.
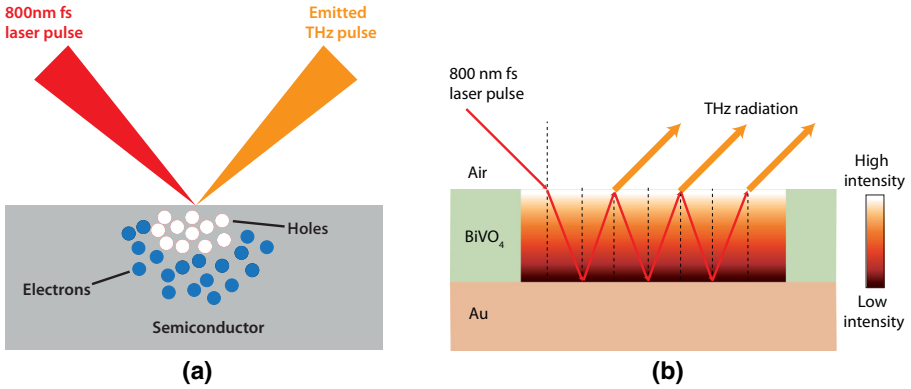
Fig. 5 **a** Schematic representation of longitudinal Photo-Dember effect, which arises due to the concentration gradient and different mobility of charge carriers. **b** Intensity distribution in the vertical direction due to the formation of standing wave pattern. The maximum intensity is at air/ $BiVO_4$ interface whereas the minimum is at $BiVO_4$/Au interface

Similar results are observed with thicker layers of silica sandwiched between gold and $BiVO_4$. This is shown in Fig. 4e where we plot the measured THz electric field emitted from an additional set of three $BiVO_4$/SiO_2/Au samples as a function of time, where the silica thickness is 5, 10, and 20 nm.

The above results make it less likely that the THz generation is due to carrier acceleration in the depletion field associated with the $BiVO_4$/Au Schottky interface. Excitation of $BiVO_4$ thin films deposited on a glass substrate using femtosecond laser pulses does not produce any measurable THz emission. This excludes the possibility of THz emission due to a surface depletion field or the surface photo-Dember effect [29–32]. We propose a new generation mechanism based on the longitudinal photo-Dember effect. The mechanism of a typical longitudinal photo-Dember effect is schematically shown in Fig. 5a. In a typical longitudinal photo-Dember effect, electron-hole pairs are generated in the vicinity of a semiconductor surface by photo-excitation forming a concentration gradient. Due to a difference in mobilities, electrons and holes move with different velocities. As a result, a dipole perpendicular to the surface is formed which emits THz radiation. Alternatively, the longitudinal Photo-Dember effect may also be realized in a slightly different way. When 800 nm laser light is incident on the $BiVO_4$ thin film deposited on gold, due to the interference of incident light and light reflected from the gold surface, a standing wave is formed. This standing wave has a low intensity at the metal surface, a consequence of Maxwell's boundary conditions, and an increasing intensity further away from the metal surface. Because of this, we have a higher absorption near the $BiVO_4$/air interface and, as a result, more carriers than near the $BiVO_4$/Au interface. In this way, we get a concentration gradient which, combined with a difference in the mobility of electrons and holes, gives rise to a THz emitting transient dipole. In $BiVO_4$, the hole mobility is higher than the electron mobility [33] (In a typical photo-Dember effect, as shown in Fig. 5a, the mobility of electrons is greater than the mobility of holes). When the optical thickness of the beam path within $BiVO_4$ approaches $\lambda/4$, the layer
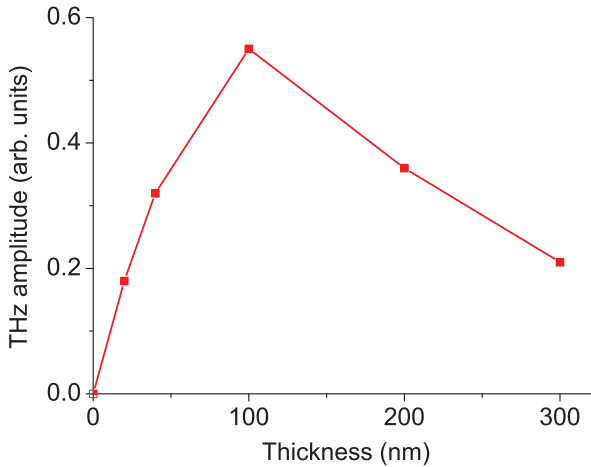
Fig. 6 THz emission amplitude from $BiVO_4$/Au for different thicknesses of the $BiVO_4$ layer

begins to act like an antireflection coating, trapping more light inside the layer and giving rise to more absorption, as we recently observed for several semiconductors on gold substrates [5]. Assuming that the metal behaves like a perfect metal, we calculate that the $BiVO_4$ thickness for which the coating acts like an antireflection coating at 800 nm is about 71 nm, assuming a refractive-index of 2.9 for the $BiVO_4$. This is thinner than the thickness (100 nm) where we observe a maximum in the emitted THz amplitude (as discussed below). The most likely explanation for this is that the deposited $BiVO_4$ layer thickness is only approximately known and might be different from 100 nm.

To further test whether the standing-wave induced photo-Dember effect provides a plausible explanation for the THz emission, we have also studied samples in which the gold layer has been replaced by indium tin oxide (ITO). ITO is a conducting oxide which reflects THz light and transmits light with a wavelength of 800 nm quite well. In the absence of the gold layer, multiple reflections are strongly reduced and no significant charge carrier gradient is formed. As a consequence, no THz emission is observed when the gold layer is replaced by ITO layer. This provides supporting evidence for our proposed generation mechanism of THz radiation from the $BiVO_4$/Au interfaces.

In Fig. 6, we show the amplitude of the THz radiation emitted from the $BiVO_4$/Au interface as a function of the thickness of the $BiVO_4$ layer. When we increase the thickness of the $BiVO_4$ thin film, the THz emission initially increases with increasing thickness, peaks around 100 nm and then decreases. The results suggest that as we increase the thickness of $BiVO_4$ thin film, the absorption of pump light increases which is expected as the interaction length of the pump light with $BiVO_4$ increases (Lambert-Beer law). More absorption leads to the generation of more charge carriers, and, as a result, the THz amplitude increases. As we further increase the thickness of $BiVO_4$ layer, the absorption becomes high and less light reaches the gold surface.

As a result, the standing wave is much less pronounced and so the THz amplitude decreases again.

4 Conclusion

In conclusion, we demonstrate THz emission from $BiVO_4$/Au thin film interfaces and investigate the possible generation mechanisms using THz radiation. Based on the experimental results and observations, we propose that the longitudinal photo-Dember effect is the mechanism responsible for the THz generation.

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