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THz-near IR hyper-Raman surface spectroscopy of silicon wafer surface

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We recorded the hyper-Raman spectra resulting from the interaction of picosecond visible and ultrashort THz pulses at the surface of (111) silicon wafer. It reveals the signature of the Si lattice phonon and SiO₂ mode centered at $\sim 610 \text{ cm}^{-1}$ and $\sim 1100 \text{ cm}^{-1}$, respectively. This technique also evidences the growing of the SiO₂ layer at the surface of the silicon wafer exposed to ambient air.

I. INTRODUCTION

THz induced second harmonic generation is a well known technique making it possible to record second harmonic generation (SHG) in a centrosymmetric material such as silicon [1]. At the surface of silicon different processes have been shown to account for THz induced SHG [2]–[4]. The generated field writes $E_{\text{SHG}}(2\omega \pm \Omega) \sim \chi^{(3)}(\omega, \omega, \Omega, 2\omega \pm \Omega) E(\Omega) E^2(\omega)$ where $E(\Omega)$, $E(\omega)$ and $\chi^{(3)}(\omega, \omega, \Omega, 2\omega \pm \Omega)$ are the electric field of the THz and optical pulses and the third-order susceptibility of the studied material, respectively. This indicates $E_{\text{SHG}}(2\omega \pm \Omega)$ results from a hyper-Raman scattering process. It is strongly enhanced when one of the frequencies in $\chi^{(3)}(\omega, \omega, \Omega, 2\omega \pm \Omega)$, for instance Ω , is resonant with the studied material [5]. Hence, for a broadband THz pulse, the enhancement of the SHG spectra at a frequency $2\omega \pm \Omega_1$ is the signature of resonant mode of the material at Ω_1 . Hereafter, we use this technique to reveal the IR active modes at the surface of a Si(111) silicon wafer. We also shown this technique can be used to reveal the growing of the SiO₂ layer at the surface of the silicon wafer.

II. EXPERIMENTAL SET-UP

The experiment was performed using a 3.5 mJ Ti:Sapphire regenerative amplifier that yields at 1 kHz repetition rate, 50 fs pulses centered around 800 nm. A 1 mJ pulse is used to generate ultrashort THz pulse through a two-color plasma generation. The generated THz pulse is transmitted by a 1 mm thick silicon wafer, collimated and focused on the (111) silicon wafer by two off-axis parabolic mirrors. On the silicon wafer set at an angle of incidence of 45°, the p-polarized THz pulse is mixed colinearly with a 2 μJ s-polarized optical pulse spectrally narrow ($\Delta\lambda \sim 40 \text{ nm}$) centered at $\sim 800 \text{ nm}$ whose pulse duration is $\sim 500 \text{ fs}$ Full Width at Half Maximum (FWHM). The optical pulse, passing through the last focusing off-axis parabolic mirror, is focused on silicon wafer by a lens with a focal length $f=125 \text{ cm}$. A delay line makes it possible to delay the optical and THz pulses with respect to each other. The SHG signal generated on the silicon wafer is detected by a photomultiplier set at the exit of a monochromator. To evidence the evolution of the SHG signal versus the delay between the optical and THz pulses, the THz pulse is chopped at 500 Hz and the SHG signal recorded by the photomultiplier is recorded by a lock-in amplifier. The SHG spectra is also recorded by a thermally cooled CCD camera at the exit of a spectrometer. The

spectral resolution for this experiment is determined by the spectrograph and the bandwidth of the near IR optical pulse

III. RESULTS

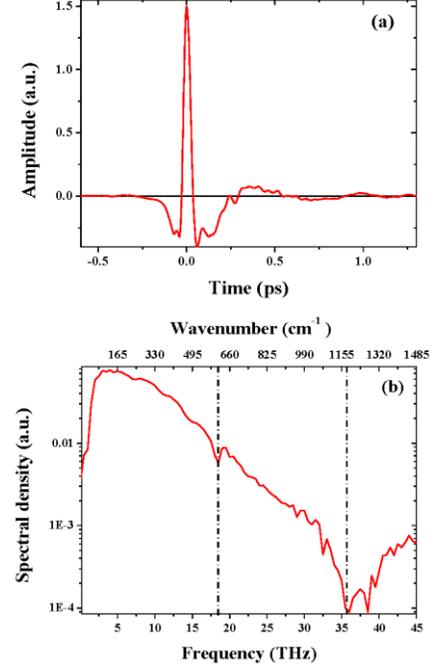


Fig. 1. Temporal shape and spectra of the THz pulse used to perform the THz-IR hyper-Raman experiment.

Prior to the experiment, we measured the electric field of the THz pulse and its spectrum (Fig.1). The generated THz pulse is short ($\sim 60 \text{ fs}$) and its spectrum centered about 5 THz spans up to 45 THz. It also reveals two IR absorption bands which are induced by the silicon wafer used to filter the THz pulse from the remaining radiations emitted by the plasma. These bands are centered about 18.5 THz ($\sim 610 \text{ cm}^{-1}$) and 35.4 THz ($\sim 1100 \text{ cm}^{-1}$). They are related to Si lattice phonons and the absorption by interstitial oxygen in crystalline silicon [6].

Firstly, we recorded the evolution of the THz induced SHG signal detected by the photomultiplier as we delayed the THz pulse with respect to the optical pulse. Its FWHM is $\sim 520 \text{ fs}$, close to the FWHM of the optical pulse.

Then we set the delay between the optical and THz pulses to optimize the SHG and record the SHG spectra. The latter displayed in Fig. 2a exhibits a sharp and narrow peak centered at $\sim 399 \text{ nm}$ and a Stokes and anti-Stokes band shifted by $\sim 11 \text{ nm}$. When the THz pulse is blocked the latter disappears while the peak centered at 399 nm remains. This indicates the central peak results from SHG at the air-silicon interface, while the Stokes and anti-Stokes bands results from difference- and sum-frequency between the THz and second harmonic spectral components. The two sharp dips in the Stokes and anti-Stokes

bands are reminiscent of the dips in the spectrum of the THz pulse used to perform our experiment (Fig.1b). Hence their shifts in wavenumber are very close the one displayed in Fig. 1b. The Stokes and anti-Stokes shift of $\sim 610 \text{ cm}^{-1}$ is associated to the resonance of the third order susceptibility for THz spectral component centered around the Si lattice phonon frequency.

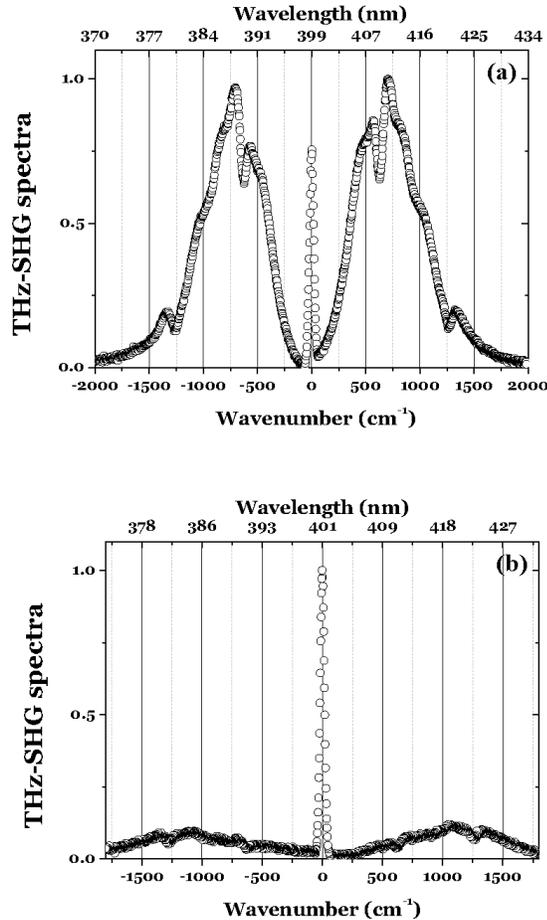


Fig. 2. Spectra of hyper-Raman spectra of the fresh and exposed few days in ambient air silicon wafer.

Afterwards, the silicon wafer was kept in ambient air. After few days, we run the experiment and recorded the spectrum displayed in Fig. 2b. Compared to Fig. 2a, the amplitude of the Stokes and anti-Stokes bands are strongly reduced and their maximum is shifted towards 1100 cm^{-1} (i.e. towards the ‘reststrahlen’ band of SiO_2 lying in between $950\text{--}1300 \text{ cm}^{-1}$). This indicates the contribution of the Si lattice contribution to the THz-SHG is strongly reduced. It is well known that when exposed to air a SiO_2 layer grows at the surface of the silicon. In ambient air and at $T=570 \text{ }^\circ\text{C}$, the growing of the SiO_2 thickness can be up to $0.7 \text{ }\mu\text{m}/\text{hour}$ [7]. This thickness has to be compared to the coherence length L_c of the THz-SHG in reflection in silicon which is $L_c \sim 0.072 \text{ }\mu\text{m}$. Accordingly, and even if at the room temperature the growing rate of the SiO_2 is much lower, we estimated, that the strong reduction of the Si lattice phonon Stokes and anti-Stokes bands is likely related to the growing of the SiO_2 layer at the top of the silicon wafer.

IV. SUMMARY

In conclusion, we reported for the first-time surface hyper-Raman spectroscopy combining an ultra-short THz pulse with a near IR picosecond pulse. This technic is used to reveal the IR active Si lattice phonon and the growing of the SiO_2 layer at the top of the Si surface. It is worth mentioning this promising surface sensitive technic can be easily used to characterize the IR active modes of almost all solid and liquid interfaces.

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