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LIGHT DEPOLARIZATION EFFECTS IN TIP ENHANCED RAMAN SPECTROSCOPY OF SILICON (001) AND GALLIUM ARSENIDE (001)

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ABSTRACT. We report on the effects of light depolarization induced by sharp metallic tips in Tip-Enhanced Raman Spectroscopy (TERS). Experiments on Si(001) and GaAs(001) crystals show that the excitation field depolarization induces a selective enhancement of specific Raman modes, depending on their Raman tensor symmetry. A complete polarization analysis of the light backscattered from the tip confirms the TERS findings. The spatial confinement of the depolarization field is studied and its dependence on the excitation wavelength and power are explored.

1. Introduction

Tip-Enhanced Raman Spectroscopy exploits plasmon resonances, localized at the apex of metallic tips, to enhance and confine the electromagnetic field on the 10nm scale [1, 2]. Polarized TERS offers additional opportunities for signal contrast increase [3, 4, 5], nano-crystallography [6] and studies of the molecular arrangement at the nanoscale [7]. A detailed knowledge of the local electromagnetic field is, however, required to assess current results.

To this aim we have carried out a complete polarization analysis to determine the Stokes vector and the degree of polarization (DOP) of the light scattered from the tip, for s-polarized excitation at two wavelengths (458 and 514.5 nm)[8]. We find that gold tips convert the totally polarized laser field into a partially polarized one, and that the light scattered at 514.5 nm is less polarized (DOP=0.5) than the one scattered at 458 nm (DOP=0.75). Moreover, about 20% percent of the s-polarized excitation is transformed into p-polarized one. Similar results are found at 633nm [9].

2. Results and Discussion

A striking consequence of the excitation field depolarization is the selective enhancement of the T_{2g} Raman mode at 520 cm^{-1} ($\times$20 amplification), with respect to the 2-phonons mode at 980 cm^{-1} ($\times$3.5 amplification), that can be observed comparing the polarized TERS spectrum of Si(001) (Fig. 1, black line, tip in contact with the surface)

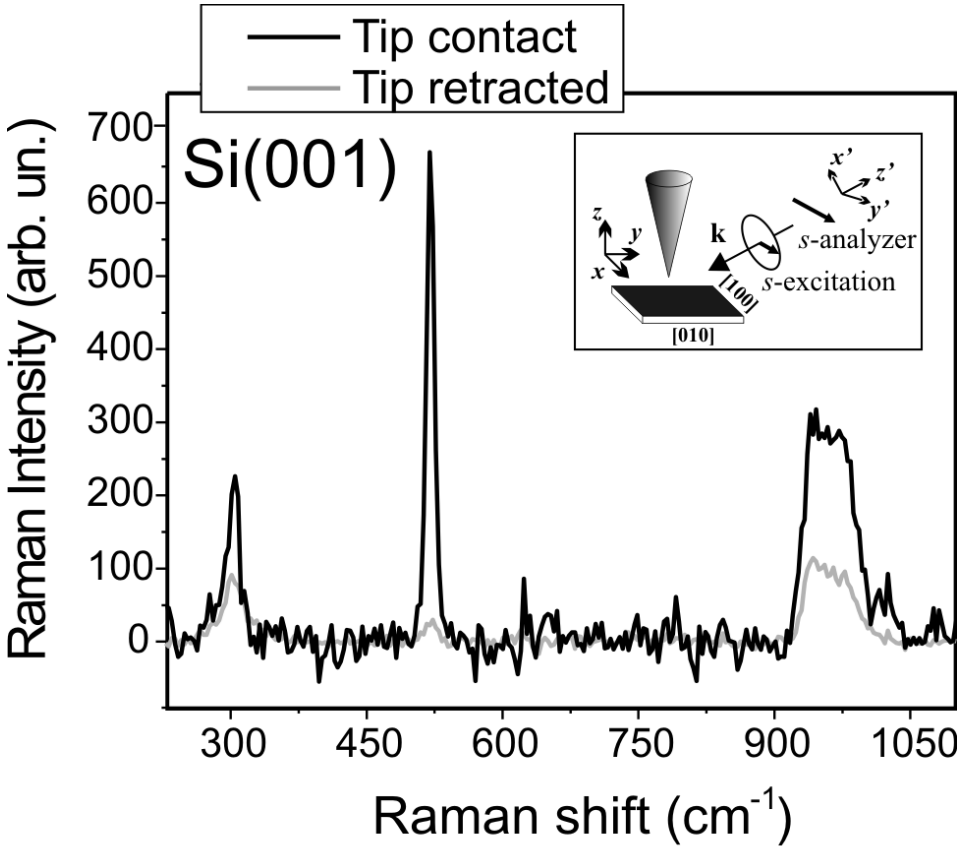


Figure 1. TERS spectrum of Si(001) (black line) compared to the Raman spectrum (grey line). In both cases the s-polarized component of the Raman scattering is acquired with an excitation field s-polarized.

with the corresponding Raman spectrum (Fig. 1, grey line, tip retracted by several microns) [8, 9, 10]. In both cases we use s-polarized excitation, with field parallel to the [100] crystallographic axis, combined with detection of the s-polarized component of the Raman scattering. This configuration is of particular interest since it permits to suppress by a factor higher than 10 the Raman scattering at 520 cm^{-1} (Fig. 1, grey line) when the tip is far from the sample, the so-called far-field background in TERS [4, 5]. Given the different symmetries of the two modes [4, 11] we can attribute the enhancement of the T_{2g} mode to depolarization and the 2-phonons mode to field enhancement [8, 10]

Similar results were found for GaAs(001) [12] in which we measure a $\times 5.6$ enhancement of the LO-mode at 292.5 cm^{-1} in the TERS spectrum (Figure 2, green line) with respect to a $\times 1.6$ enhancement the TO-mode at 270 cm^{-1}. The two modes, again, feature different polarizability tensors.

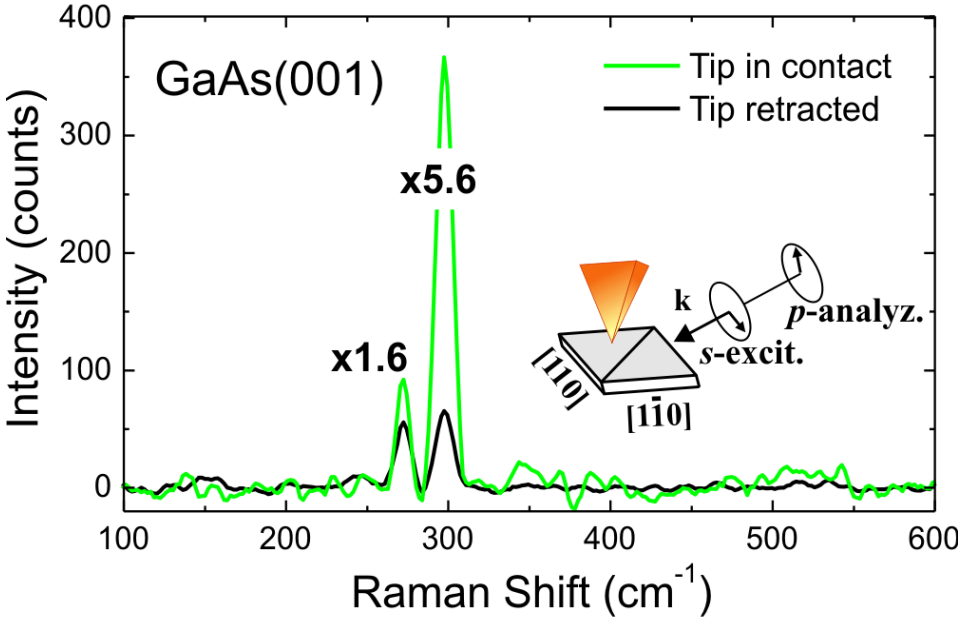


Figure 2. (green line) TERS spectrum compared to Raman spectrum (black line) of GaAs(001). In both cases the sample is excited with an s-polarized field, parallel to the [110] crystallographic axis, detecting the p-polarized component of the Raman field.

By monitoring the TERS intensity Vs the tip-sample distance we show that the depolarized field extends over several hundreds of nm. We find that the effect is power-dependent with a threshold at around 3 mW [8]. Beam deflection due to scattering from the tip shaft is also shown to play a relevant role in the interpretation of the signals [12].

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