Vacuum 110 (2014) 102–105

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Interference enhanced first-order Raman band of monocrystalline silicon

Ľubomír Vančo, Magdaléna Kadlečíková, Juraj Breza*, Jaroslava Škriniarová, Pavol Hronec

Slovak University of Technology, Ilkovičova 3, 812 19 Bratislava, Slovakia

ARTICLE INFO

Article history:
Received 21 June 2014
Received in revised form
5 September 2014
Accepted 6 September 2014
Available online 16 September 2014

Keywords:
SiO_2/Si structure
Raman spectroscopy
SERS
Interference
Enhancement factor

ABSTRACT

In the present study we discuss how excitation and Raman scattered wave interference enhances the intensity of the dominant Raman band of silicon (520.7 cm^{-1}) measured in backscattering configuration. We applied the formalism of the transfer matrix for a normal incident laser beam onto the SiO_2/Si structure and proposed the calculation of the enhancement factor. We confronted theoretical values with an experiment on a prepared SiO_2/Si structure. Twofold enhancement of the intensity of the 520.7 cm^{-1} band was achieved. Experimental results for low numerical apertures (0.25) are in agreement with theoretical predictions and the theory could be generalized to two-layered structures. For higher numerical apertures (0.75 and 0.95) the supposition of normal incidence is not valid any more, thus observable deviations are introduced to the enhancement factor.

1. Introduction

The origin of the dominant Raman band in monocrystalline silicon is well understood. It is driven by the first order phonon scattering in the center of the Brillouin zone and by the selection rule $|\mathbf{k}| \approx 0$. The frequency of the band [1,2] is given by the phonon frequency in the Brillouin zone center (Γ) equal to 15.56 THz, which is equivalent to 520.7 cm^{-1}. The dominant band is triple degenerated because three optical phonons are present with symmetry $\Gamma_{25'}$ [1,3]. More nuances of the scattering process are usually described via Feynman diagrams: (a) an impinging photon generating an electron (hole) which is scattered by an optical phonon, recombines and releases energy in the form of a Stokes or anti-Stokes photon, (b) an incoming photon generating (annihilating) a phonon which immediately releases energy in the form of a Stokes (anti-Stokes) photon. The latter is a less probable process, whereas the former is generally considered as a dominant mechanism due to resonance scattering [4].

If the material under study is covered by a capping layer, m-fold ($m \rightarrow \infty$) reflection subsequent to excitation will occur from the boundaries. The phase of the electric wave depends on the thickness of the capping layer, angle of incidence and complex reflection coefficients. The amplitude of the m-times reflected wave inside the layer is m-times gradually decreased, and the total outcome of all m waves converges to a finite value. The principle was successfully utilized in interference-enhanced Raman spectroscopy of superstrate thin films [5–8], and recently a dramatic effect of interference on the Raman spectrum of graphene superstrate [9–11] has been shown. Unlike these examples, we studied interference enhancement of the Raman signal of the silicon substrate in Si/SiO_2 structure. It constitutes an appropriate object to study the impact of interference upon the Raman signal because the structure can be easily prepared, the optical constants of these materials are easily measurable or well known and, which is important, the pertinent band has a narrow bandwidth (depending on spectrometer parameters, in our case the measured value was ~3.5 cm^{-1} FWHM) thus it is not necessary to integrate the intensity over frequency.

The aim of the present study is to clarify the enhancement of Raman bands caused by constructive interference of light. Interference is achieved with the help of a capping layer which is transparent for the exciting laser wave and deposited *above* the monitored layer. Our work differs from the published papers on interference effects in Raman spectra because they deal with the effects in capping layers deposited *below* the monitored layer. We also believe that the interference enhancement can be the source of additional enhancement applicable in the surface-enhanced Raman technique. To describe the interference effects upon Raman spectra, we have employed the SiO_2/Si structure. It can be easily prepared by standard methods as it is one of the most important structures used in semiconductor technology.

* Corresponding author.
E-mail address: juraj.breza@stuba.sk (J. Breza).

http://dx.doi.org/10.1016/j.vacuum.2014.09.004
0042-207X/

2. Experimental

Monocrystalline (111)-oriented silicon wafers from MEMC, St. Peter (USA) with 150 mm diameter, phosphorus doped with resistivity 5.0–15.0 Ωcm (dopant concentration 3–9 × 10^{14} cm^{-3}) and thickness 655–695 μm were used as a substrate for deposition of the SiO_2 layer. Deposition was performed, without preliminary treatment of wafers, in plasma enhanced chemical vapor deposition apparatus Oxford PlasmaLab 80 with silane and nitrous oxide as precursors (flow ratio 85:710 in sccm). The holder temperature was 300 °C ± 10%, and the working pressure reached 133 Pa. In total, fifteen depositions with different thicknesses of oxide were carried out. The thickness and refractive index of the deposited oxide were determined by ellipsometry. Parameters Ψ and Δ in the range 250–1100 nm acquired under 55° illumination and 2 nm step using Angstrom Advanced PhE-102 spectroscopic ellipsometer were fitted to tabulated dielectric values of SiO_2 [12].

Ten Raman spectra were acquired in backscattering geometry on each sample in the center of the structure and the average intensity and related standard deviation of the 520.7 cm^{-1} band were determined. To avoid the effect of imperfect focusing, each spectrum of the ten was acquired as the maximum of the depth profiled spectra in the range of several tens or units of micrometers, measured three times and averaged automatically by Labspec software. Dispersive Raman spectrometer JobinYvon Labram 300 with a 632.8 nm He–Ne laser was used with illumination power 17 mW. The impact of three different numerical apertures (NA) was investigated and series of measurements were repeated using 10 × (NA = 0.25), 80 × (NA = 0.75) long-working distance, 100 × (NA = 0.95) objectives.

In Raman measurements, NA has a considerable effect on the intensity of Raman spectra since it is inherently connected with the objective strength and thus with the monitored volume and irradiated surface. Roughly, the intensity of Raman signal increases with NA although the irradiated surface decreases. Also the angle of the rays in the excitation beam is changed, which can affect the measurement.

Then the band intensity on a reference sample (naturally oxidized (111)-oriented silicon wafer) was measured in the same fashion. Then the ratios of band intensities on the prepared samples and reference samples were calculated with related standard deviations. We adopted the thickness of natural oxide (approx. 2 nm) as a generally accepted value.

The structure examined in the experiment and considered theoretically was of type given in Fig. 1 with complex refractive indices n_1, n_2 and n_3 of materials 1, 2 and 3, with capping layer thickness x.

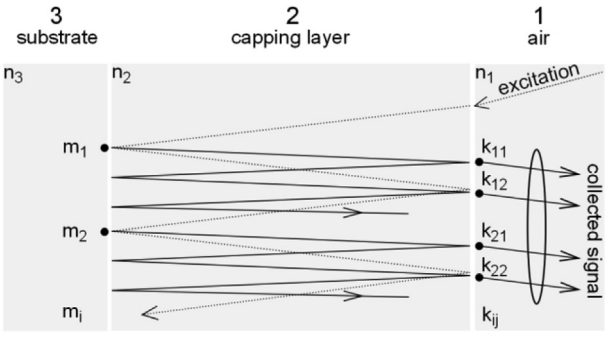

Fig. 1. Material ordering and schematic of incident and scattered wave interference in oblique incidence.

3. Results and discussion

3.1. Raman scattering in SiO_2/Si structure

The scattering process in oblique incidence is shown in Fig. 1. The incoming wave transmits through the 1-2 interface and experiences multiple reflection-transmission events reaching points m_i, $i = 1,2,3 \ldots$ Points m_i are sources of Raman scattered radiation which takes place in all directions and phases. The sum of scattered waves at each point m_i can be substituted by a corresponding wave in opposite direction. The same process as with the incoming wave occurs with the scattered m_i point's wave, reaching points k_{ij}, $j = 1,2,3 \ldots$ We account for three differences between excitation and the scattered wave: different wave vector, different starting amplitude and reverse sequence of the layers to be propagated through. All waves coming to points m_i can be understood as solitary waves transmitted through 1-2, affected by multiple reflections between 2-1 and 2-3 and transmitted through 2-3 and similarly, the same is for waves at k_i in reversed order. We recall that the angle between the surface normal and the direction of the incoming wave is to be zero and each of points in m_i series and k_{ij} series are located at only spatial coordinates. The process can adopt the transfer matrix formalism.

The enhancement factor *EF* is defined as a dimensionless ratio of Raman band intensities measured on the examined sample and on the reference sample. So as to calculate the enhancement factor of the 520.7 cm^{-1} Raman band of silicon as a function of the capping layer thickness x it is necessary to assume the following simplifying suppositions:

(a) Refractive indices of natural oxide and deposited oxide are unvaried and equal to n_2.
(b) The electric wave intensity subsequent to Raman scattering and measured in backscattering direction is the same at each point of the silicon surface and proportional to the amplitude of the impinging electric wave with proportionality constant K for a given objective.
(c) K is small enough, which allows neglecting further Raman scattering.
(d) The change of phase $\Delta\varphi$ of the measured scattered wave is the same at the reference sample and at the prepared samples.
(e) Layers 1 and 3 are infinite in the direction outwards from layer 2.
(f) The thickness of the deposited oxide layer is homogenous and the surface is smooth. We consider the reflections to be specular.

The transfer matrix applied to an optical cavity [13] with length x and a normal incident beam leads to equation.

$$\begin{pmatrix} E_1^+ \\ E_1^- \end{pmatrix} = \mathbf{M^{12}M^2M^{23}} \begin{pmatrix} E_3^+ \\ E_3^- \end{pmatrix} = \mathbf{M} \begin{pmatrix} E_3^+ \\ E_3^- \end{pmatrix} = \frac{1}{t_{12}t_{23}} \begin{pmatrix} e^{i\delta} + r_{12}r_{23}e^{-i\delta} & r_{23}e^{i\delta} + r_{12}e^{-i\delta} \\ r_{12}e^{i\delta} + r_{23}e^{-i\delta} & r_{12}r_{23}e^{i\delta} + e^{-i\delta} \end{pmatrix} \begin{pmatrix} E_3^+ \\ E_3^- \end{pmatrix} \quad (1)$$

where E terms are affined with notation in Fig. 2 and, for brevity in the sequel, they relate only to the amplitudes of waves. $\mathbf{M^{12}}$ is the transfer matrix for interface 1-2, $\mathbf{M^2}$ is the transfer matrix for homogenous 2nd layer, t_{12} and r_{12} are transmission and reflection coefficient of interface 1-2 and analogically for $\mathbf{M^{23}}$ one has t_{23}, r_{23}