Journal of ELECTRICAL ENGINEERING, VOL. 52, NO. 3-4, 2001, 101–103

COMMUNICATIONS

RAMAN SPECTROSCOPY —– A POWERFUL ANALYTICAL TECHNIQUE FOR MICROELECTRONIC INDUSTRY

Ján Janík — Alexander Kromka *

We present ex-situ Micro-Raman monitoring of the surface temperature of silicon wafers. The induced Raman shift (RS) and the full width at half-maximum (FWHM) of the silicon line have been measured in temperature range from 20 to 350 °C at air conditions. The Raman signal was collected from the back side of silicon, thus from a relatively rough surface. The obtained results revealed a linear dependence of the line shift and of FWHM on temperature. A possible use of RS as an *ex-* and/or *in*-situ technique working at various environment conditions is briefly viewed, where RS is shown as a powerful technique becoming "widely" used in monitoring and control of the growth processes for microelectronic industry.

K e y w o r d s: contact-less temperature measurement, silicon, Raman

1 INTRODUCTION

Precise and reproducible process control plays a key role in microelectronic industry. One of the most important parameters in the growth of thin films (TF) is the substrate temperature. The measuring of "true" surface temperature of the substrate surface is not a simple and easy task. Physical and/or chemical vapor deposition (PCVD) processes are mostly carried out in harsh and hostile environments, which are *i*) aggressive or *ii*) not-acceptable for placing the measuring probe in. The standard methods like *i*) *thermocouple method* (contact method, the thermocouple is placed on the back side of the substrate and does not measure the true substrate temperature due to the temperature gradient across the bulk of the substrate) or *ii*) *infra-red method* (non-contact method which is limited by the unwanted background emission) are not satisfactory for PCVD processes used in microelectronic industry.

The industrial requirements are to use a technique which *i*) minimally influences the "TF growth environments" and *ii*) is sensitive enough to the measured signal. Raman spectroscopy is one of promising techniques which could satisfy the conditions described above. The Raman effect belongs to a class of molecular-scattering phenomena. It is based on inelastic light-scattering arising from the interactions of photons with lattice vibrations or phonons. Lattice vibration is Raman active when the vibration changes the polarizability of molecules. Some photons could be emitted from the induced oscillating dipoles, which are either of the *same frequency* as the incident beam (*elastic Rayleigh scattering*) or have been *frequency shifted* by an amount equal to the vibration frequency of the lattice (*inelastic Stokes or anti-Stokes scattering*). The shifted frequency is attributed to the Raman scattering which was named after Sir C.V. Raman, who discovered the effect in 1928 [1]. The Stokes scattering (the normal Raman effect) is produced when energy is extracted from the light beam to the crystal and sets it into vibration, whereas the anti-Stokes scattering arises from the annihilation of the existing thermally-excited vibration. What is most important, the vibration modes are dependent on the *atomic bonding type and an arrangement of the matrix*.

In this paper we present a dependence of the Raman line-shift and FWHM of silicon on its temperature. The obtained results indicate a linear dependence of the Raman response in the measured temperature range.

2 EXPERIMENTAL

The surface temperature was measured by the K-type thermocouple and by Raman spectroscopy, Fig. 1. The thermocouple was placed on the front side of a non-polished silicon wafer. The silicon wafer was resistively heated up to a temperature of 350 °C and then cooled down in air conditions. Micro-Raman measurements were performed using ISA Labram equipment (Jobin/Yvon//Spex/Dilor, Horiba Group) installed at the Department of Microelectronics FEI STU, Bratislava [2]. This spectrometer operates with the 632.817 nm line from a HeNe laser in the backscattering geometry. A "×50" microscope objective was used to focus the laser onto a spot of approximately 1 μm in diameter and to collect the scattered light, which then passed through the spectrometer onto a CCD detector. Furthermore, a confocal hole with a diameter of 200 μm, a spectrograph entrance slit of 150 μm, and a 1800 grooves/mm diffraction grating were employed.

* Department of Microelectronics, Slovak University of Technology, 812 19 Bratislava, Slovakia, E-mail: jjanik@elf.stuba.sk

ISSN 1335-3632 © 2001 FEI STU

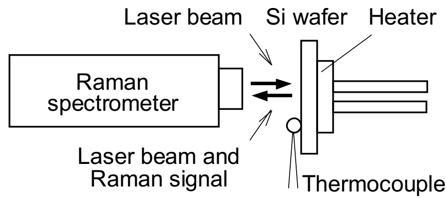

Fig. 1. Schematic view of temperature measurement setup

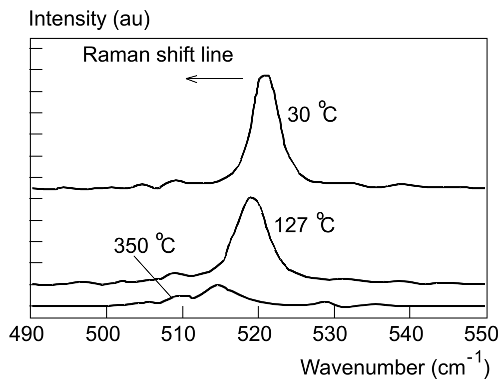

Fig. 2. Raman spectra of Si wafer as a function of temperature

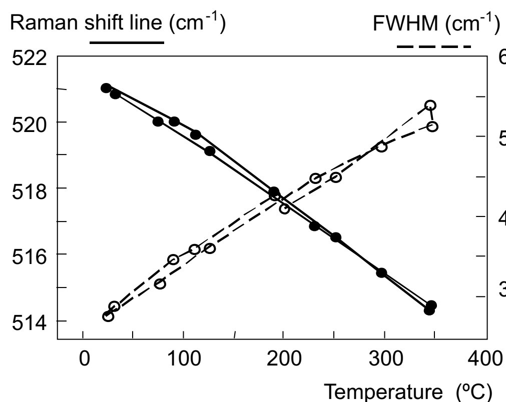

Fig. 3. Raman shift and FWHM of silicon line *vs* temperature

All spectra were recorded using the same laser power and integration times and are presented without making any offset or scaling of the data. It is important to note that all data were fitted using software LabSpec V2.08 (fy. DILOR). Automatic calculation of the baseline was applied with deviation value of 0.5 %. (The deviation is to say the residual difference between the calculated baseline and the optimal one). All spectra were fitted to Gaussian/Lorentzian curves by computer deconvolution of the data points and each of the peak positions was determined automatically.

3 RESULT AND DISCUSSION

Figure 2 presents Raman spectra of a Si wafer for three different temperatures, 20, 127 and 350 °C, respectively. It could be observed that *i*) the Raman characteristic line of silicon shifts to lower wave number values with increasing temperature (T_{Si}), *ii*) the FWHM becomes broader with increasing T_{Si}, and *iii*) the area below the Raman line decreases as T_{Si} increases.

The dependence of the Raman shift and of FWHM of the Si line is shown in Fig. 3. Small "hysteresis" in the Raman shift and FWHM is observed for temperature increase and decrease. The different results the heating up and cooling down are assumed to be caused by "non-stability" of the system during its heating up (nonlinearity is observed mainly during heating up). This is because the system has been tested in the "fast response reliability" (Raman measurement for $\sim$ 10 s) and the thermocouple was not able to follow the changes in temperature within 10 s. The measurements during cooling down (by self cooling in the lab) are stable and linear, which could be explained via long time temperature stabilization (cooling down was slower).

The observed results are in good agreement with the calculations made by Cowley [3] and the measurements made by Hart *et al* [4]. In a simple model, we can imagine that the increasing of temperature causes an increase of the amplitude of atom oscillations from the off positions and the Raman line shifts to a lower value of the wave number (= to higher frequencies). However, a more appreciative explanation requires quantum-mechanical calculations of the potential energy of atoms [3, 4]. The FWHM as a function of temperature could be written [4] as

$$\mathrm{FWHM}(T) = \mathrm{FVHM}(0)\Big(1 + \frac{2}{\exp\frac{\eta\omega_0}{2k_BT} - 1}\Big) \qquad (1)$$

where T is the sample temperature, k_B is the Boltzmann constant, and $\mathrm{FWHM}(0) = 2.1\,\mathrm{cm}^{-1}$ corresponds to a mean free life time of $\tau = 2.5\times10^{-12}$ s. Our data fit this curve in its "linear region", *ie* for temperatures above 0 °C.

These results demonstrate that a relatively simple and fast technique could be used in determining the true surface temperature. In the case of unwanted radiation (for example from plasma), we must use a pulsed laser beam operating in a synchronized mode with the detector. In such an arrangement, the detector is only active for the duration of the laser pulses, and the intensity of the pulsed Raman signal is increased in comparison with the continuous light from the plasma. Thus the amount of "background" emission is reduced to a negligible level as compared with the Raman signal [5]. Furthermore, the actual surface temperature could be calculated also from the

intensity ratio of Stokes ($I_{\rm St}$) and anti-Stokes ($I_{\text{anti-St}}$) Raman lines, which is written as [6]

$$\frac{I_{\rm St}}{I_{\text{anti-St}}} = \Big(\frac{v_l - v_0}{v_l + v_0}\Big)^4 \exp\Big(\frac{hv_0}{k_b T}\Big) \tag{2}$$

where v_l is the central frequency of the excitation source, v_0 is the phonon frequency, and h is the Planck constant.

It is also well know that the Raman shift line depends also on *induced stresses* into the bulk of thin films. Therefore, we have to be careful in identifying the true substrate temperature during the thin film growth. However, this is not our case. In such a case, the measurement of intensity ratio of Stokes and anti-Stokes Raman lines could be very powerful and the surface temperature could be calculated from this ratio [6].

The main advantages of Raman spectroscopy are: *i*) non-destructive and non-contact nature *ii*) relatively fast (required time 1–10 s), *iii*) does not require sample treatment, *iv*) acceptable for any environments and does not require vacuum conditions, and *v*) able to scan micro-dimensions. For the microelectronic industry, Raman spectroscopy can provide a lot of useful information about: *i*) true surface temperature and induced stresses in thin films (Raman shift *vs* temperature), *ii*) crystallographic quality (crystal size and order *vs* FWHM), *iii*) impurities and chemical composition (position of Raman line) and *iv*) semiconductor conductivy type (comparison of LO and TO line intensities, luminescence shift, *etc*). Furthermore, Raman spectroscopy is used in detection and identification of chemical and biological materials, in geology (gases in rocks), pharmacy (drugs) and environment measurements (gas composition), which are not discussed here in detail due to a lack of space.

The main disadvantages of RS are: *i*) possible damaging of temperature sensitive samples (by "too high" laser beam irradiation), *ii*) detection limit for continuos thin films with a thickness of tens of microns, *iii*) technological requirements on laser system and optics (UV, VIS, macro sample imaging) and *iv*) requires an optical access for the incident laser beam and the collector of the scattered light.

CONCLUSIONS

Non-contact and non-destructive measurement of temperature of a Si wafer was performed by Raman spectroscopy. A non-polished Si wafer was heated up to a temperature of 350 °C and then cooled down in air conditions. As calibrated by the thermocouple, the Raman line-shift and FWHM showed a linear dependence in the measured temperature range. Finally, the main advantages and disadvantages of RS for microelectronic industry were summarized. RS was shown as a promising analytical technique with multifunctional uses not only for the scientific community but also for industrial and commercial uses in the Slovak Republic.

Acknowledgement

The authors would like to express their thanks to Mr. Š. Bederka for his support and permanent interest. We are indebted to Mr. J. Král for technical assistance. This work has been supported through the grant project No. 95/5195/327 of the Slovak Republic.

References

[1] RAMAN, C. V.—KRISHNAN, K. S.: Nature **121** (1928), 501.

[2] MALCHER, V.—MRŠKA, A.—DUBRAVCOVÁ, V.: Application of Diamond Layers for Cutting Tools in Mechanical Engineering (Aplikácie diamantových vrstiev pre rezné nástroje v strojárstve), Strojárstvo **4** (2000), 72–74. (in Slovak)

[3] COWLEY, R. A.: J. Phys. **26** (1965), 659.

[4] HART, T. R.—AGGARWAT, R. L.—LAX, B.: Physical Review **B1** No. 2 (1970), 638.

[5] MEMOUX, M.—FAYETTE, L.—MARCUS, B.—ROSMAN, N.—ABELLO, I.—LUCAZEAU, G.: Phys. Stat. Sol. (a) **154** (1996), 55.

[6] HERCHEN, H.—CAPELLI, M. A.: Phys. Rev. B **43** (1991), 11740.

Received 19 February 2001

Ján Janík (Doc, Ing, CSc) was born in Handlová in 1946. He received his Ing (MSc) degree in solid state physics, in 1970 and the CSc (PhD) in applied physics, in 1981, both form the Slovak University of Technology, Bratislava. Since 1992 he has been Associate Professor in Electronics (thesis: The Methodics of Ionooptical Elements and Systems Computation) at the Departmnet of Microelectronics of Slovak University of Technology. He tought different subjects as vacuum physics and technology, optoelectronics, microwave technology, electrical instrumentation, electron and ion technology, electronic and microelectronic elements, and microelectronic materials technology. In research he was oriented to ion beam optics and plasma technology. He spent some time at scientific stays abroad. Long-time stay in Dubna, Russia (1987-89) as a member of Cyclotron Design Group, then in CERN, Switzerland (1993-94) as ion-beam optics designer for the AUSTRON project and six short-time stays in GSI Darnstadt, Germany (1992-96) as ion-beam optics designer for a medical accelerator. He collaborate on hadron therapy project, sponsored by oncology 2000 in Czech Republic.

Alexander Kromka (Ing), born in Nitra in 1971. He received his MS degree in electronic engineering from the Slovak Technical University, Bratislava, in 1995. He has been a PhD student at the Department of Microelectronics of the Faculty of Electrical Engineering and Information Technology, since February 1996. His research interests include diamond thin films deposition techniques and its application for microelectronic devices. He spent 3 months at Institut für Festkörper Elektronik in Ilmenau, Germany, in 1995, where he worked on the project Multilayered and Quasi-Superlattice Structures for Sensors and Photovoltaics in the field of the investigation of AlN and SiC thin films.