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Technology and micro-Raman characterization of thick meso-porous silicon layers for thermal effect microsystems

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Abstract

Thermal effect microsystems (TEMS) need a highly thermally insulated substrate. Porous silicon (PS) offers promising applications for insulation of thermal transducers from silicon wafers as its thermal conductivity is close to that of silicon oxide. A thorough investigation of PS thermal conductivity has been carried out regarding its technological parameters, i.e., porosity, thickness and oxidation temperature, by means of micro-Raman spectroscopy which yielded thermal conductivity values less than 2 W/m K as predicted by theoretical considerations. For TEMS, a 100-μm-thick meso-PS layer with a porosity of about 50% and oxidized at a moderate temperature (300°C) presents the best attributes to ensure both an efficient thermal insulation, as its thermal conductivity value was found to be 0.6 W/m K, and a good mechanical strength.

Keywords: Porous silicon technology; Thermal insulation; Micro-Raman spectroscopy

1. Introduction

Thermal effect microsystems (TEMS) such as IR detector, flow sensor, etc., require a reliable thermal insulation of their sensing elements from the silicon substrate to provide efficient and accurate measurements. The CMOS-compatible insulating substrates used up to now are mostly microstructures combining low thermal conductivity materials, such as silicon oxide and/or silicon nitride, to micromachined freestanding monocrystalline silicon structures [1,2]. The resultant membranes or cantilever beams have a low effective thermal conductance reducing the thermal flux between the "hot" sensing zone of the TEMS and its "cold" reference rim but present poor mechanical properties.

Porous silicon (PS), whose thermal conductivity is close to that of silicon oxide, obtained by anodic etching of monocrystalline silicon offers a good alternative for the thermal insulation of TEMS. Firstly, it requires a simple fabrication process which may exhibit a high CMOS compatibility. A tissular blood microflow microsensor based on thick oxidized meso-PS thermal insulation was lately achieved [3]. Standard CMOS technological steps, such as low-temperature oxidation (LTO), chemical vapor deposition (CVD), implantation and annealing were carried out. Polysilicon thermistors and polysilicon/aluminum thermopile were deposited on top of the meso-PS layer and successfully tested. In addition, the fabrication process of thick PS layers of over 100 μm thickness takes only several minutes compared to hours needed to form a few micrometers thick SiO_2 layers by thermal oxidation of silicon. Secondly, studies carried out during the past 5 years have brought to light the low value of PS thermal conductivity [4–7], which, however, strongly depends on the physical parameters of the layer. As presented Table 1, nano-PS has a lower thermal conductivity than meso-PS but its fragile "sponge" nanostructure [8] does not withstand high-temperature processes as meso-PS does. Therefore, meso-PS has been so far preferably used in TEMS fabrication processing. Besides, when increasing the porosity of the meso-PS layer, its thermal conductivity decreases (Table 1), whereas its mechanical strength decreases. So a technological compromise needs to be found, which re-

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Table 1
Thermal conductivity of non-oxidized PS layers, at room temperature

Authors	Type of PS	Initial monocrystalline silicon wafer	PS layer thickness (μm)	PS layer porosity (%)	Thermal conductivity (W/m K)
Benedetto et al. [6]	Meso	p^+, ⟨111⟩	10	50	3.9
			23	60	2.5
Gesele et al. [5]	Nano	p, ⟨100⟩	31	64	0.18
	Meso	p^+, ⟨100⟩	21	64	0.8
Our work	Meso	p^+, ⟨100⟩	50	50	0.7
			100	70	0.3

quires a thorough knowledge of PS thermal characteristics regarding its technological parameters (porosity, thickness and oxidation).

Consequently, we have carried out systematic measurements of the meso-PS thermal conductivity regarding process parameters by means of an original and recently proposed technique using micro-Raman spectroscopy [9]. This direct and non-contact method, compared to those based on photoacoustic spectroscopy [6] or propagation of electrical-induced thermal waves [5], was successfully applied as features of Raman spectra are often directly correlated to thermal properties of materials [10,11]. In this paper, we report for the first time on our experimental results: surface PS thermal conductivity as a function of the layer oxidation temperature, porosity and thickness.

2. Sample preparation

The meso-PS layers were obtained from a p^+, ⟨100⟩-oriented, 0.02 Ω cm monocrystalline silicon substrate using a preparation process already described [2]. The samples were electrochemically etched in an electrolyte solution (50% HF and ethanol in a ratio 1:1). For all samples, the current density during the etching process remained constant. Meso-PS layers of 5, 50 and 100 μm thickness and with 50% and 70% porosities were studied. Measurements were first achieved on as-prepared samples. Then all samples were oxidized successively at 150°C, 300°C and 450°C for 1 h and their thermal conductivities were measured after each annealing step.

3. Measurement method

A heating power source focused on the sample surface generates a thermal gradient through the material depending on its thermal conductivity. Assuming a very shallow heat generation and that the studied layer thickness is at least equal to the heating source diameter, a simple linear relationship [12] combining the heating power P and the local temperature rise T_j can be used to derive the material thermal conductivity κ:

$$\kappa = \frac{2P}{\pi a\left(T_j - T_b\right)}, \tag{1}$$

where T_b is the bulk temperature, a the heating source diameter. Heat losses in the air are assumed to be negligible and the distribution of the isotherms within the layer to be hemispherical.

Using two complementary effects encountered in micro-Raman experiments (Fig. 1), T_j and thus κ can be determined [9]. The first one is local superficial heating caused by laser light absorption in the sample. The resulting temperature rise is directly related to the medium thermal conductivity. The second effect is a shift of the Raman peak with temperature [13–15] that can be used to deduce the local temperature rise. Indeed, the Raman peak position shifts towards lower wave numbers when increasing local temperature.

Then a calibration performed in a large temperature range — at low heating power so as not to induce additional heating — results in a linear relationship between the Raman peak position and T_j [9].

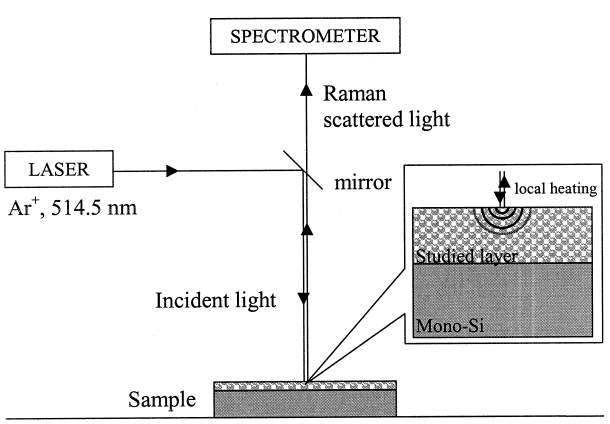

Fig. 1. Experimental set-up of the micro-Raman-spectroscopy-based measurement method of the thermal conductivity of thin layered materials. A local heating is created on the surface of the studied layer, inducing hemispherical isotherms.

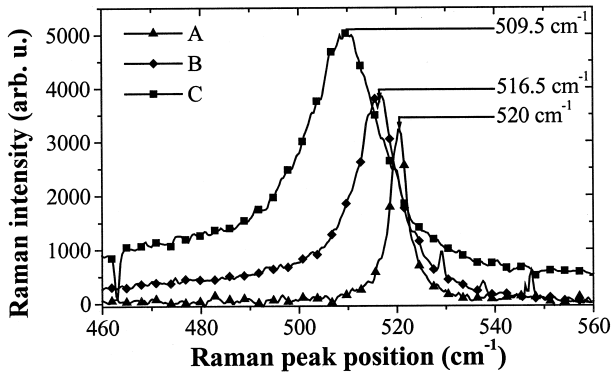

Fig. 2. Raman peak spectra at room temperature of: (A) p^+-type monocrystalline silicon, $P = 2$ mW; (B) PS, $P = 2$ mW; (C) PS, $P = 5$ mW.

So knowing the laser heating power and the local temperature rise, the layer thermal conductivity can be found in Eq. 1.

Micro-Raman scattering was excited by a 514.5-nm line of an Ar^+ laser at normal incidence. The micro-Raman backscattered spectra in parallel polarization were recorded using an Olympus BH2 microscope (objective $\times 50$) coupled with a Dilor XY monochromator and a cooled photodiode array detector (Gold Dilor). The power distribution of the laser beam has a Gaussian nature. However, a constant mean value of the laser diameter was assumed to be $a = 5$ μm.

Thermal conductivity evaluation was achieved, taking into account the main random error that is the uncertainty on the Raman peak position estimated to be ± 1 cm^{-1}.

Fig. 2 illustrates the Raman peak shift dependence on the material thermal conductivity and on the heating power P. Spectra A and B were recorded for a 2-mW heating power on p^+-type monocrystalline silicon (A) and meso-PS (B), respectively. Spectrum C was obtained on the same meso-PS sample for a 5-mW heating power. At the same heating power $P = 2$ mW, the low thermal conductance of meso-PS engenders a higher surface temperature than with bare silicon. The local temperature rise is also directly related to the incident heating power when recorded on the same sample.

Practically, in order to get rid of the bulk temperature measurement, differential measurements were performed on the same sample spot, i.e., Raman spectra were recorded for two different heating power P_1 and P_2, resulting in two local temperature T_{j_1} and T_{j_2}.

4. Meso-PS thermal conductivity vs. oxidation temperature

Measured thermal conductivities on as-prepared samples were found to be already of the order of that of silicon oxide, known as a good thermal insulator. The drop of the thermal conductivity from 150 W/m K for monocrystalline silicon to a few watts per meter Kelvin for meso-PS layers can be explained by the confinement effect of the phonons within the crystallites, as proposed by Lysenko et al. [7] in an already published model. This model predicts that meso-PS thermal conductivity is largely influenced by the silicon crystallites size, the layer porosity and the oxidation fraction.

Fig. 3 depicts the evolution of the surface thermal conductivity of two 100-μm-thick meso-PS layers of 50% and 70% porosity after three 1-h oxidation annealings. Thermal conductivity of both samples presented the same dynamics. For oxidation temperature under 300°C, their thermal conductivity decreased with increasing temperature down to a minimum κ_{min}, 0.6 and 0.3 W/m K for the 50% and 70% porosity samples, respectively. This thermal conductivity minimum was predicted by the model of Lysenko et al. [7] and already indirectly observed by photoacoustic spectroscopy measurement. Because of the oxidation process, the size of the silicon crystallites in the columns is reduced and the thermal conductivity of the columns becomes lower than that of the non-oxidized columns.

Then thermal conductivity slightly increased for oxidation temperature above 300°C. This rise is mainly due to the growth of silicon oxide gradually filling all air pores and hence, leading to bulk silicon oxide layer of 1.5 W/m K thermal conductivity.

For oxidation temperature considerably lower than 300°C, meso-PS columns are not sufficiently oxidized and thus, do not guarantee the layer chemical stability during further high-temperature technological process and the layer thermal conductivity is higher than κ_{min}. For oxidation temperature much higher than 300°C, high mechanical constrains within the layer due to the increasing silicon oxide volume neither guarantee the mechanical stability of the meso-PS nor the $\kappa_{meso\text{-}PS} > \kappa_{min}$. Consequently, the oxidation process at moderate temperature (about 300°C) allows to adjust the lowest thermal conductivity value of the meso-PS layer and to guarantee its structural and mechanical stability. So this process finalizes the thermal insulating substrate to be used for the TEMS.

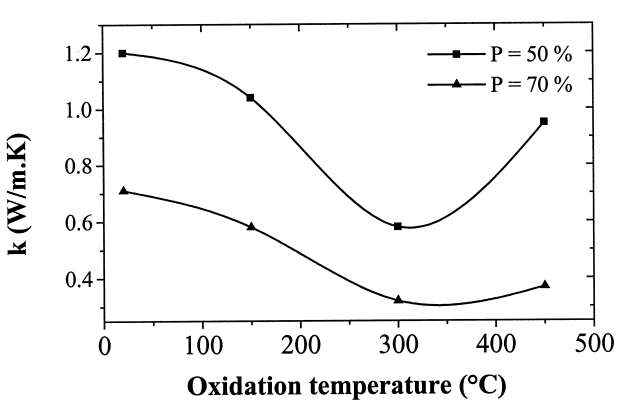

Fig. 3. Thermal conductivity of 100-μm-thick meso-PS layers of 50% and 70% porosity vs. temperature of each 1-h post-xidation process.

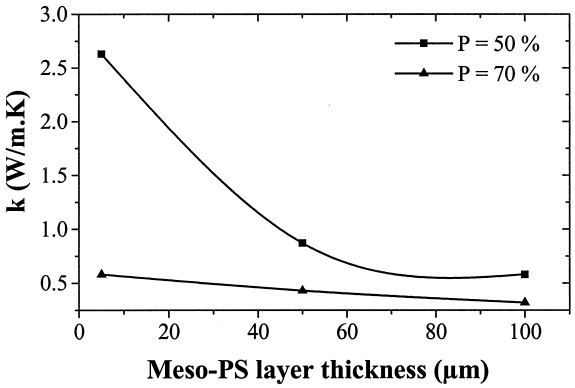

Fig. 4. Thermal conductivity of 300°C oxidized meso-PS layers of 50% and 70% porosity vs. the layer thickness.

Finally, as shown Fig. 4, the thermal conductivity decreased with increasing porosity. However, we have observed that meso-PS layers with 50% porosity guarantee better mechanical strength of the microstructure than layers with 70% porosity. Hence, it should be preferably used to ensure the thermal insulation of TEMS.

5. Meso-PS thermal conductivity vs. layer thickness

Surface thermal conductivity of 300°C oxidized meso-PS layers was then investigated as a function of the layer thickness for two porosities. We assumed that the thermal conductivity was constant along the layer thickness.

Fig. 3 presents the evolution of meso-PS thermal conductivity with the layer thickness and confirms anew that the lowest thermal conductivity values are obtained for enhanced porosity samples.

As shown in Fig. 3, the surface thermal conductivity of both series of samples decreased with increasing layer thickness. The drop is more significant for the 50% porosity samples as the thermal conductivity of the 5-μm-thick, 70% porosity sample is already less than 1 W/m K. However, for both series, thermal conductivity decreased by a factor of about 3.

Measurements performed on the 5-μm-thick layers reached the limit of our experimental conditions as the laser beam and the layer thickness were of the same order. The induced surface temperature rise does not only depend on the meso-PS layer but also on the silicon substrate. The isotherms are then neither longer totally confined in the meso-PS layer nor hemispherical. However, the inaccuracy on these experimental values is acceptable for thermal conductivity assessment.

Whatever the layer porosity, meso-PS layers present a column structure [16,17]. But the thicker the layer is, the more chaotic the thermal path along the columns is, which tends to decrease the layer thermal conductivity.

For the 70% porosity samples, this latter effect still exists, which explains the decrease of the thermal conductivity value. However, for enhanced porosity, the effect of the porosity on the thermal conductivity value is accentuated by the thickness effect. Columns can be represented as small Si/SiO_2 crystallites fitted in [7]. Then the phonons confinement effect within the crystallites is emphasized, which implies thermal conductivity value lower than 1 W/m K even for thin layers.

Anyway, the meso-PS layer has to be thick enough (> 100 μm) to ensure the lowest thermal conductivity value and to increase the thermal resistance of the layer. Even though thick enhanced porosity samples have a thermal conductivity less than 1 W/m K, thick 50% porosity meso-PS layers are preferred for the thermal insulation of TEMS because of their better mechanical stability.

6. Conclusion

We have shown that a thick meso-PS layer, over 100 μm thick, oxidized at moderate temperature (about 300°C) and of a mean porosity, typically 50%, guarantees an efficient and reliable thermal insulation for thermal microsystems applications.

The measurement technique based on micro-Raman spectroscopy gives an excellent estimation of PS thermal conductivity and allows us to determine the best technological compromise to achieve meso-PS layers for its thermal insulating applications in TEMS realization. Furthermore, because it is a direct and non-contact method, Raman scattering appears as a successful non-destructive diagnostic tool for thermal characterization of TEMS. Additionally, it allows surface or cross-section mapping of the thermal conductivity for production process optimization.

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Biographies

Stéphanie Périchon was born in 1975 in France. She received her Electrical Engineering diploma and her MS on Integrated Electronic Devices in June 1998 from the National Institute of Applied Sciences (INSA) in Lyon, France. She was involved in the validation of a behavioral simulator to model TEMS. Since September 1998, she has been working on her PhD at the Laboratoire de Physique de la Matière, LPM, at INSA de Lyon, France. She is in charge of the conception and the design of thermopiles deposited on thermally insulating substrates to realize microcalorimeters.

Vladimir Lysenko was born in 1973 in Ukraine. He received his MS degree in Solid-State Electronics in 1995 from National T. Shevchenko University, Radiophysical Faculty, Semiconductor Electronics Department, Kiev, Ukraine. In the period 1992–1995, he worked as an engineer assistant on the design of semiconductor potentiometric biosensors in the Bioelectronics Laboratory of the National T. Shevchenko University. From 1995 to 1998, he was a PhD student at National T. Shevchenko University (Kiyo, Ukraine) and the Ecole Centrale de Lyon (France). He studied new semiconductor materials and devices for the design of thermal microsensors to be applied in biomedical and medical fields. In 1998–1999, he carried out a Post-Doctorate at the National Institute of Applied Sciences (INSA) in Lyon, France where he worked on thermal properties of porous silicon.

Philippe Roussel was born in 1970 in France. He received his MS degree in Biomedical Engineering in 1996 from the University of Lyon I, France. Since 1996, he has been a PhD student at the National Institute of Applied Sciences, Lyon, France. His thesis work is focused on the design of a thermal microsensor for in vivo tissue microcirculation measurements.

Boudjemaa Remaki was born in 1955 in Algeria. He received his Electrical Engineering diploma in 1980 from the National Institute of Applied Sciences (INSA, Lyon, France). He obtained a PhD on Electronics Engineering and Semiconductors in 1985 from the same institute. He joined the Electrical Engineering Department of Lyon University in 1988 as Associated Professor (Maitre de Conférences). He was involved in research on solid-state sensors for 9 years (1988–1997). Since 1997, he has been in charge of silicon-based microsensors research at the LPM (Laboratoire de Physique de la Matière) of INSA/CNRS. He is the author of about 20 publications dealing with study and research on new materials for electronic and sensor devices.

Bernard Champagnon was born in 1948 in St. Etienne France. He studied Physics in the University of Lyon where he received its “These of 3ème cycle” in 1971 and a “Doctorat d’état” in 1979. He is currently professor at the Université Claude Bernard, leader of a research group on amorphous materials and semiconductor nanostructures in the LPCML (Laboratoire de Physico-Chimie des Matériaux Luminescents). He is a specialist on Raman spectroscopy in the field of low-frequency inelastic scattering and in micro Raman techniques.

Daniel Barbier was born in 1950. He received an engineering degree from the Institut National des Sciences Appliquées de Lyon, France, and the Engineer-Doctor and the Doctor ès Science degrees from the Claude Bernard, Lyon I University between 1973 and 1985. Initially specializing in low-thermal-budget annealing and processing techniques for microelectronics and photovoltaics, he is currently leading a group at the Laboratoire de Physique de la Matière, INSA de Lyon, working on silicon microtechnologies. He has authored or co-authored more than 80 papers, the latest concerning the technology, characterization and modeling of active microstructures for pressure microsensors or microbiosensors.

Pierre Pinard was born in 1933. He received the Doctor ès Science degree in 1964. He has been a University Professor since 1968. He started his scientific career working on scanning electronic microscopy (pioneer on analysis based on cathode luminescence). Then he worked on defects in semiconductors. Since 1980, his research has been dealing with silicon microelectronics and also microsystems and microtechnologies (since 1990). He was the head of the Laboratoire de Physique de la Matière at INSA, Lyon, France, from 1966 to 1995. He is now the director of the Research at INSA. He is the co-founder member and executive board member of the EMRS. He is the author of about 200 international publications and communications.