Photothermal radiometric and spectroscopic measurements on silicon nitride thin films

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Thin films of silicon nitride of various thicknesses, deposited by radio frequency magnetron sputtering on silicon quartz substrate, have been characterized by laser-induced and frequency scanned photothermal radiometry. Fourier transform infrared spectroscopy was also used to provide a qualitative description of the behavior of the films in the infrared range which shows favourable properties of these coatings to be used in passive cooling applications. © *1997 American Institute of Physics.* [S0021-8979(97)03024-7]

I. INTRODUCTION

In the last few years as the demand for advanced materials and especially electronic devices has grown dramatically, new material characterisation techniques have been developed to meet this demand. The noncontact character of the photothermal techniques makes them particularly attractive for nondestructive evaluation (NDE)[1,2] of materials. The photothermal radiometry (PTR), which allows the measurement of the optically induced emission of blackbody radiation from the surface of a material, is a powerful characterisation technique.[3–5] During the last few years PTR has been applied to a great extent, for the characterisation of implanted silicon wafers,[5–8] thin film structures,[4,6,9] dielectric on semiconductor structures,[10] as well as for the imaging of biological samples.[11,12] Tam and Sullivan[13] have also used photothermal radiometry for remote sensing applications, while Guitonny *et al.*[14] used the same technique for detection of cracks on steel samples. In this work the PTR technique is employed for the characterisation of samples which are used as passive cooling surfaces.[15–17] Passive cooling is a mechanism of emission of thermal energy from a surface, exposed to the clear sky, in a particular wavelength band (8–13 μm), known as the atmospheric window.[17] In this wavelength band, the transmittance of the atmosphere is very large, provided that the humidity is quite low, so the emitting surface can lower its temperature[15–17] below the ambient temperature. Several suitable materials[15,16] are under investigation, for example one can cite: silicon-based coatings backed by metal, metallized polymer foils, gas slabs backed by metal and ceramic oxide layers. In this paper we examined thin films of silicon nitride samples using photothermal radiometry.

II. EXPERIMENTAL DETAILS

Thin silicon nitride films of different thicknesses have been deposited by RF magnetron sputtering from high purity silicon nitride (Si_3N_4) target, in an atmosphere of argon at a pressure of 3×10^{-3} Torr. The residual pressure in the deposition chamber was about 3×10^{-7} Torr. The substrate temperature was 100 °C. The films were deposited on n-type Si $\langle 100\rangle$ ($\rho=10-30\ \Omega$ cm) substrates (200 μm thickness), and on quartz substrates, Herasil 1 (500 μm thickness) which combines excellent physical properties with outstanding optical characteristics in the ultraviolet (UV) and visible wavelength range. Before their introduction in the deposition chamber, the silicon substrates were cleaned in HF (5%), to remove the native surface oxide. The thickness of the films was measured by a profilometer. The approximate thicknesses of the films deposited on both silicon and quartz substrates, are presented in Table I.

PTR characterization of the samples, has been made using the experimental setup of Fig. 1. The photoexcitation source was a Coherent Innova I308 Ar^+ gas laser emitting at wavelengths of 488 and 514.5 nm. The beam diameter was 3 mm with an output power of 180 mW. The intensity of the laser was acousto-optically modulated using a Bragg cell, connected to an external sine-wave generator, which was used to change the modulation frequency.

The blackbody radiation emitted from the semiconductor was collected by means of two collimating, off axis, Ag coated, paraboloidal mirrors and was focused onto a wide bandwidth, liquid nitrogen-cooled, photoconductive HgCdTe

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TABLE I. Thickness and absorptivity of the silicon nitride thin films at the pump beam wavelength.

Sample	Thickness (Å)	Absorptivity
MB107	1000	0.37
MB106	1700	0.46
MB94	3000	0.62
MB105	5000	0.73

(MCT) detector with a spectral response range between 2 and 12 μm. The MCT detector/preamplifier circuit had a combined frequency bandwidth in the range of $1-10^6$ Hz. The detector was fitted with a Ge window, which filtered out the excitation beam. The PTR signal from the preamplifier (EG&G Judson Model PA-350) was fed into a lock-in analyser (EG&G Model 5302) which was interfaced to an automatic data acquisition system from where aquiried. Placing infrared (IR) selective filters in front of the detector, it was possible to measure the PTR signal, in several distinct IR bands.

III. RESULTS AND DISCUSSION

The PTR signal amplitude for the Si_xN_y/Quartz samples, as a function of frequency, is presented in Fig. 2. In all cases the behavior of the amplitude is purely thermal,[12,18] as can be deduced from the slope of the lines. The fact that the lines are parallel shows that the thermophysical properties of the Si_xN_y/Quartz samples, are exactly the same. The purely thermal character of the signal is an indication of the lack of electrical activity of the Si_xN_y layer as expected, since quartz is a dielectric material.

The sample with the thicker coating absorbs a greater amount of the incident energy, and therefore creates a stronger temperature field, which results in a stronger IR emission. This behavior is consistent with the results of Spicer *et al.*,[19] and can interpreted with a model which has been presented in the past.[20] This is why the sample MB105/Quartz gives the highest signal, followed by MB94/Quartz, MB106/Quartz and MB107/Quartz. The photothermal signal emitted from the quartz substrate was in the noise. From the spectroscopic measurements performed, the transmission of quartz at the pump beam wavelength was found to be more than 90%. Since there is almost no absorption, we do not expect a PTR signal from the quartz substrate. The absorptivity of the Si_xN_y coatings at the pump beam wavelength was found to vary from 0.37 (MB107) to 0.73 (MB105). The absorptivities for the several coatings, are also presented in Table I.

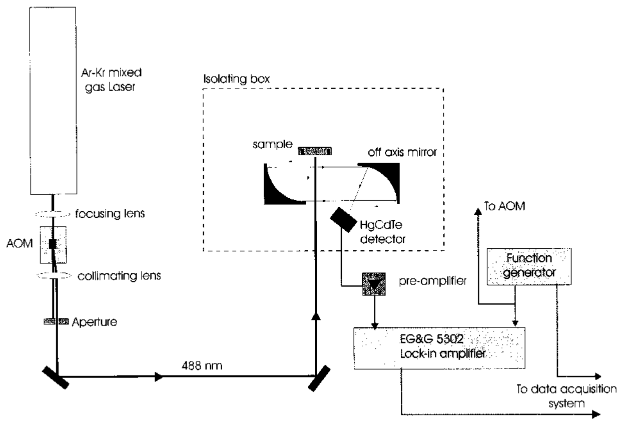

FIG. 1. The experimental setup.

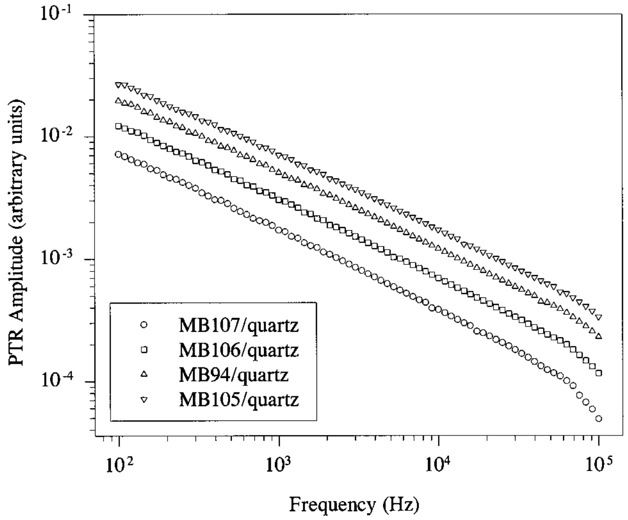

FIG. 2. The PTR amplitude as a function of modulation frequency for the Si_xN_y/Quartz samples.

The photothermal signal amplitude for the Si_xN_y/Si samples, and the silicon substrate as a function of the modulated frequency are presented in Fig. 3. The silicon substrate with its characteristic PTR signature,[3,5,12] has the highest signal. Its purely electronic behaviour is well explained in terms of the modulated hole-electron excess concentration, created due to the absorption of the pump beam photons. Sample

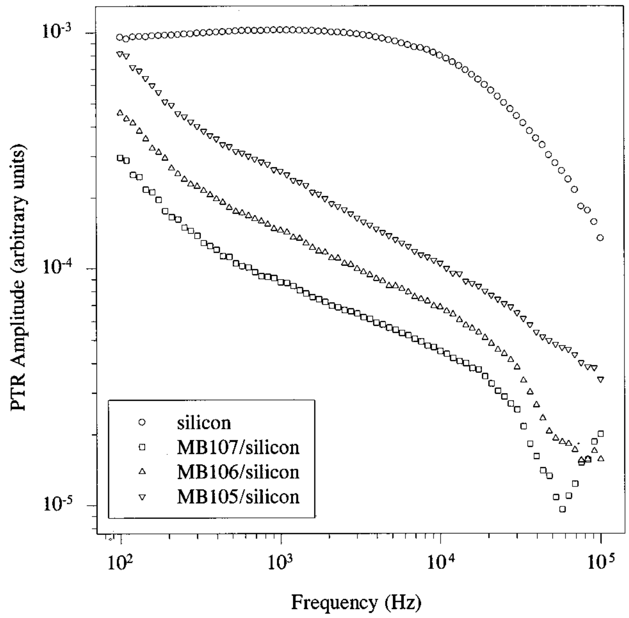

FIG. 3. The PTR amplitude as a function of modulation frequency for the Si_xN_y/Si samples.

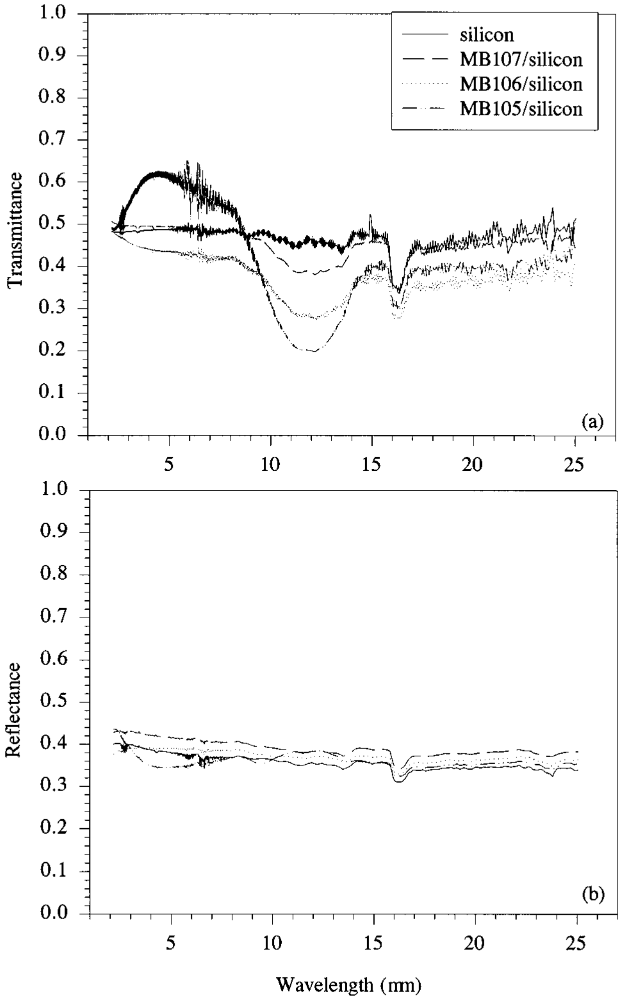

FIG. 4. FTIR data for Si_xN_y/Si samples: (a) transmission data and (b) reflection data.

MB105/Si has the strongest PTR signal among the rest of the samples, since it has the thickest coating. However the trend of the photothermal signal amplitude for Si_xN_y/Si samples is completely different from that of the films on quartz substrate. The PTR signal appears to be a combination of an electronic and a thermal contribution. The electronic contribution is more pronounced in the high frequency range ($f > 10^3$ Hz). The source of the photothermal electronic signal is without doubt the silicon substrate. In fact the electronic contribution is well damped due to the large absorption of the pump beam photons by the Si_xN_y coating, as can be deduced from Table I, and because part of the IR radiation emitted from the silicon substrate, is absorbed by the Si_xN_y coating. The last assumption can be verified from the optical behaviour of the samples in the infrared range of spectrum as seen in Figs. 4(a), and 4(b). These figures present the Fourier transform infrared (FTIR) transmission and reflection spectroscopic data for the Si_xN_y/Si samples. A pronounced absorption band in the range of 9–12 μm for the Si_xN_y coatings is clearly seen. The results, contrary to the Si_xN_y/Si FTIR data, show only a slight absorption in the 2–5 μm band.

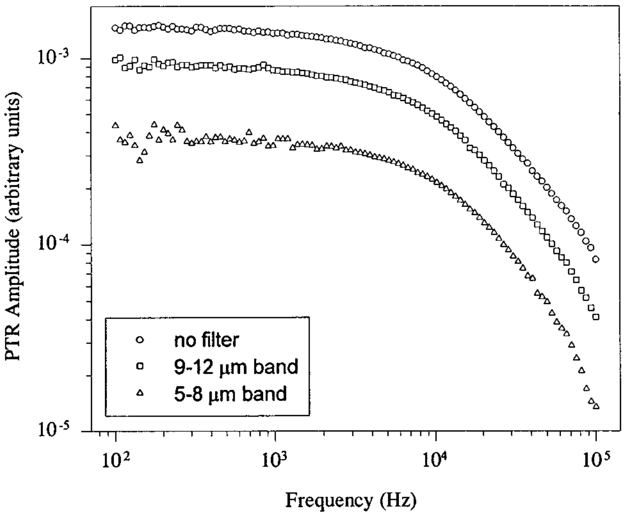

FIG. 5. Infrared spectroscopy of the silicon substrate PTR signal, with the use of infrared filters.

A PTR spectroscopic study of the silicon substrate, accomplished with the introduction of various filters in of the detector, is presented in Fig. 5. The main contribution to the photothermal signal lies in the 9–12 μm range, while a smaller contribution is in the 5–8 μm range. To further investigate Si_xN_y/Si samples, spectroscopic measurements with the above filters have been carried out on MB105/Si (see Fig. 6). We observe again that the greater proportion of the PTR signal detected is in the range of 9–12 μm and that only a small fraction of the PTR signal is emitted in the 5–8 μm range. It is important to note that the spectral response of the infrared detector has been taken into account in Figs. (5)–(7). An analogous study for sample MB105/Quartz is shown in Fig. 7. The 9–12 μm range contributes 60% to the photothermal signal, as estimated by taking the ratio of the signal in the 9–12 μm range to the total signal, and the

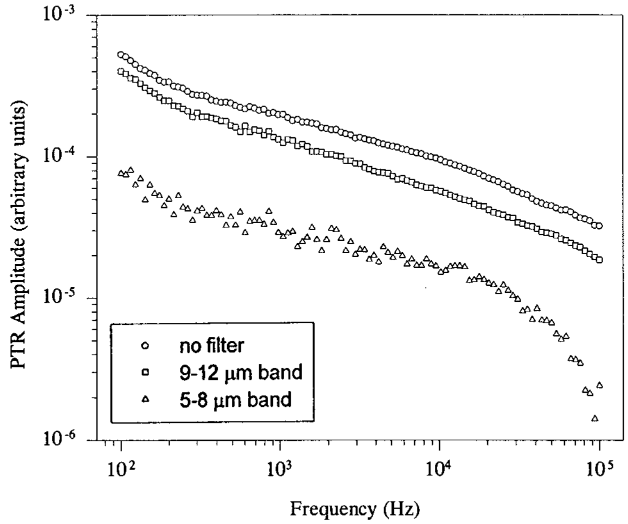

FIG. 6. Infrared spectroscopy of the MB105/Si PTR signal, with the use of infrared filters.

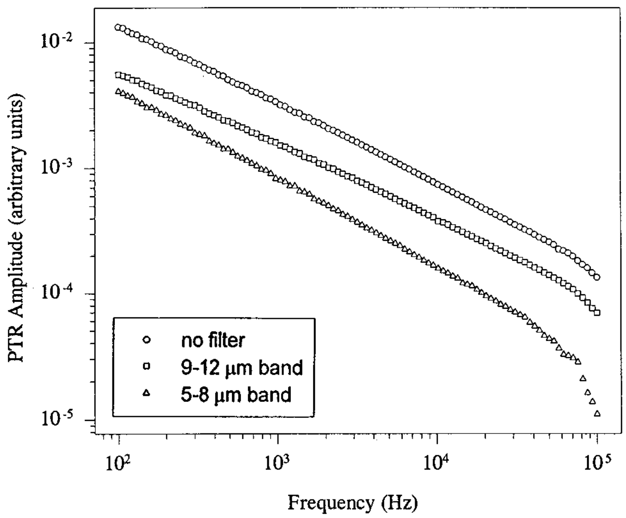

FIG. 7. Infrared spectroscopy of the MB105/Quartz PTR signal, with the use of infrared filters.

5–8 μm range the rest. It is interesting to point out that no PTR electronic behaviour is present in the above wavebands.

For purposes of comparison, the PTR results are presented in pairs of $\mathrm{Si}_x\mathrm{N}_y$/Quartz and $\mathrm{Si}_x\mathrm{N}_y$/Si samples, in Figs. 8(a)–8(c). It can be seen that the PTR electronic contribution although weak is present for all the $\mathrm{Si}_x\mathrm{N}_y$/Si samples. In addition the PTR electronic contribution of MB105/Si is more pronounced due to the large amount of laser energy reaching the silicon substrate, since the coating is very thin, which also results in a lower absorption of the silicon generated PTR signal.

Another interesting characteristic of the above group of data, is that the $\mathrm{Si}_x\mathrm{N}_y$/Quartz samples, give a PTR signal approximately 30 times higher than that of $\mathrm{Si}_x\mathrm{N}_y$/Si samples. The major sources of this great difference are the differences in thermal properties between quartz and silicon. The thermal conductivity of the quartz substrate is only $K_q = 0.0136\,\mathrm{W\,cm^{-1}\,K^{-1}}$,[21] which is almost a 100 times smaller than that of the Si[15] ($K_{\mathrm{Si}}=1.5\,\mathrm{W\,cm^{-1}\,K^{-1}}$). The thermal diffusivity of silicon ($a_{\mathrm{Si}}=0.88\,\mathrm{cm^2\,s^{-1}}$) is also 100 times greater than that of quartz, $a_q = 0.0087\,\mathrm{cm^2\,s^{-1}}$. Based on these parameters alone, the thermal wave field intensity ratio of the two materials is $K_{\mathrm{Si}}\sqrt{a_q}/K_q\sqrt{a_{\mathrm{Si}}} = 11$. To this we should also add possible differences in the reflectivity of the surfaces as well as multireflection effects between the surface and interface of the samples. The thermal properties mismatch between the coating and the quartz substrate results in the confinement of the temperature field in the coating, and thus to the emission of a strong photothermal signal.

IV. CONCLUSIONS

In this paper, PTR has been applied in order to investigate the IR emission of thin silicon nitride films deposited on quartz and silicon substrates. The purely thermal character of the former samples indicates that the silicon nitride behaves as a complete dielectric material. The electronic behaviour of the $\mathrm{Si}_x\mathrm{N}_y$/Si samples results from the contribution of the silicon substrates. The FTIR spectroscopic data showed that the $\mathrm{Si}_x\mathrm{N}_y$ layers present an absorption band in the 9–12 μm range, which fulfills the physical requirements of a passive cooling material. The PTR signal amplitude difference between the $\mathrm{Si}_x\mathrm{N}_y$/Quartz and $\mathrm{Si}_x\mathrm{N}_y$/Si resulted from the difference of the thermal properties of the substrates. The IR spectroscopic studies of the PTR signal show that the main part of the photothermal signal lies in the 9–12 μm wavelength band which coincides with the atmospheric window. This last point is important as it allows for this photothermal technique to become a major characterisation method for noncontact and nondestructive evaluation of surfaces prepared in laboratories, as well as large scale industrially produced surfaces. For example, this technique can find a direct application for the in site, real time study of the effect of surface degradation of the above samples.

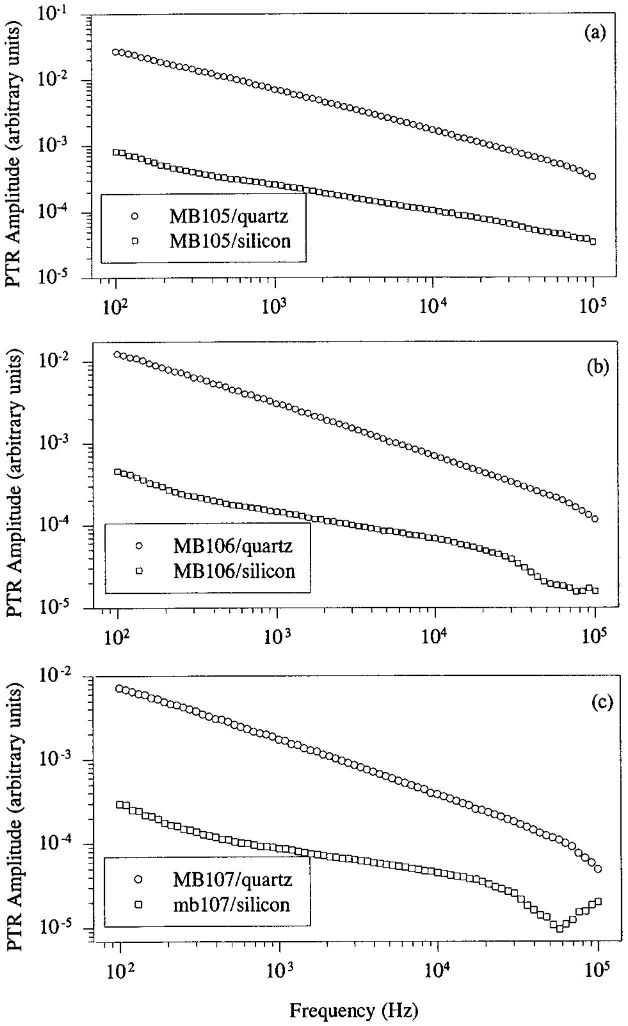

FIG. 8. Comparison of the PTR signal between same coatings on quartz and silicon substrates respectively: (a) MB105/Quartz and MB105/Si, (b) MB106/Quartz and MB106/Si, and (c) MB107/Quartz and MB107/Si.

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