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Polyimide Resists as Infrared Absorbing Layers for Radiation Microsensors

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Data on infrared radiative and thermal properties of absorbing layers are required for the design of radiation microsensors. In this paper, we describe a method based on the measurement of the spectral transmittance of a membrane using a widely available infrared spectrometer. The spectral absorptivity and the average absorptivity are mathematically deduced from this measurement. Some curves of absorptivity spectra and average absorptivity vs the thickness of a typically distributed polyimide deposit (Ultradel™) are reported.

1. Introduction

The ability to transform radiation into heat is an important problem to be taken into account for the realization of microradiometers. Thin-film materials with good absorption coefficients[1–3] are needed. Various traditional materials (Si_3N_4 and SiO_2) have been tested, but because of their weak absorption bands and their low deposited thicknesses, low sensitivities have been obtained for differential absorption microsensors developed at the laboratory.[4,5]

With the aim of optimizing the microsensors, polyimide resists seem a good alternative with improved performance for absorption because of the great thicknesses of the deposited layers of up to 20 μm. By fabricating membranes of different thicknesses, the intrinsic properties of such polyimide layers can be directly obtained.

The measurement of absorptivity at normal incidence as under real conditions is not easy. The applied method consists of recording the transmission coefficient for a large

range of frequencies with a Perkin-Elmer spectrometer. In this case, the spectral absorptivity is deduced with a simple calculation. Then the relationship between the average absorptivity in the region from 1 to 27 μm and the polyimide thickness is obtained from experimental data.

2. Method of Measurement

An infrared radiation characterized by its irradiance E that is incident on a plane parallel plate of semi-transparent material is partially reflected (R E), partially absorbed (A E) and partially transmitted (T E) (Fig. 1(a)).

The IR microradiometers produced at the laboratory are sensitive to the fraction of absorbed energy which is converted into heat (A E). To increase the sensitivities of the sensors, the spectral absorptivity coefficient must be determined.

Generally, with most spectrometers, the direct measurement of absorptivity is not possible for incident radiation. However it can be deduced from the measurement of the transmission coefficient in the simplest case where the material is processed as a membrane.

The source of emission in the Perkin-Elmer spectrometer is a tungsten filament heated to 1400 K. The detector is pyroelectric and the transmission coefficient is obtained by Fourier transform over the range 10000-370 cm^{-1} (1–27 μm).

Taking into account the multiple reflections in the polyimide membrane acting as a plane parallel plate of thickness d, the power transmission and reflection coefficients vs the wavelength λ can be written as:[6]

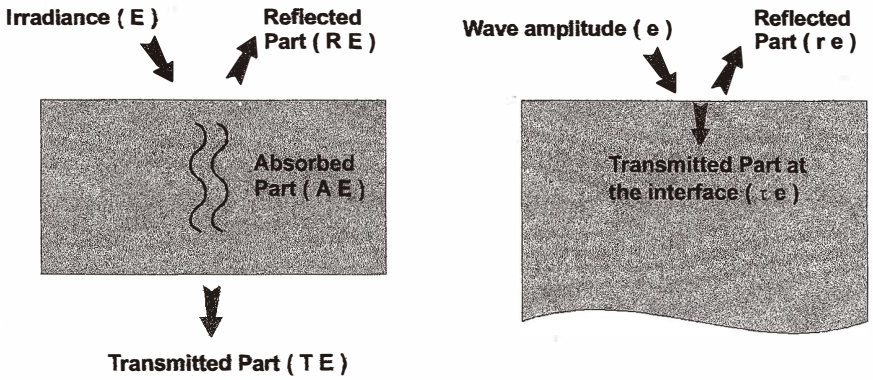

Fig. 1. (a) Energy balance in a plane parallel plate of semi-transparent material and (b) wave amplitude coefficients in a semi-infinite material.

$$T(\lambda) = \frac{t^2\tau^4}{1+t^4r^4-2t^2r^2\cos\left(\frac{2\pi}{\lambda}2\delta\right)}, \tag{1}$$

$$R(\lambda) = \frac{r^2\left[1+t^4-2t^2\cos\left(\frac{2\pi}{\lambda}2\delta\right)\right]}{1+t^4r^4-2t^2r^2\cos\left(\frac{2\pi}{\lambda}2\delta\right)}, \tag{2}$$

where, as represented Fig. 1(b):
r: the amplitude reflection coefficient at the interface of air and the semi-infinite material constituting the membrane; τ: the amplitude transmission coefficient at the same interface; $t^2 = e^{-kd}$: the power transmission coefficient into an element of material with a thickness d, where k represents the extinction coefficient; δ : the optical path difference: $\delta = nd$ where n is the ordinary index of refraction of the material.

Because there is no energy absorbed at the interface:

$$r^2 + \tau^2 = 1. \tag{3}$$

The power absorption coefficient (or absorptivity) A is deduced from the energy conservation law ($R(\lambda)+T(\lambda)+A(\lambda) = 1$):

$$A(\lambda) = \frac{\tau^2\left[1-t^4r^2-t^2\tau^2\right]}{1+t^4r^4-2t^2r^2\cos\left(\frac{2\pi}{\lambda}2\delta\right)}, \tag{4}$$

2.1 *Weak absorption regions*

In an appropriate region of the spectrum, the materials studied can be considered quasi-transparent and the incident beam traversing the sample has no significant attenuation. In this case, the extinction coefficient k is very low, the transmission coefficient t^2 of the material is close to one, and the transmission coefficient $T(\lambda)$ is given by:

$$T(\lambda) = \frac{1}{1+\frac{4r^2}{(1-r^2)^2}\sin^2\left(\frac{2\pi}{\lambda}nd\right)}. \tag{5}$$

The transmission spectrum of the membrane is represented in Fig. 2 where $\bar{\nu}$ is wave number ($\bar{\nu} = 1/\lambda$). From the value of the undulation period $\Delta\nu$ of this transmission coefficient, the thickness d of the membrane is deduced:

$$d = (2 \cdot n \cdot \Delta\nu)^{-1}. \tag{6}$$

The amplitude reflection coefficient r is given by the minimal value of the transmission coefficient T_{min} :

$$r^2 = \frac{1 - \sqrt{T_{min}}}{1 + \sqrt{T_{min}}}, \tag{7}$$

and the transmission coefficient τ at the interface can be computed from eq. (3).

2.2 *Strong absorption regions*

Into the spectral region of strong absorptions, the transmission coefficient t^2 is very low and, in this case, an approximate expression of the membrane transmission coefficient T(λ) can be written:

$$T(\lambda) = \tau^4 e^{-kd}. \tag{8}$$

In the same way, the absorption coefficient A(λ) is:

$$A(\lambda) = \tau^2(1 - \tau^2 \cdot e^{-kd}), \tag{9}$$

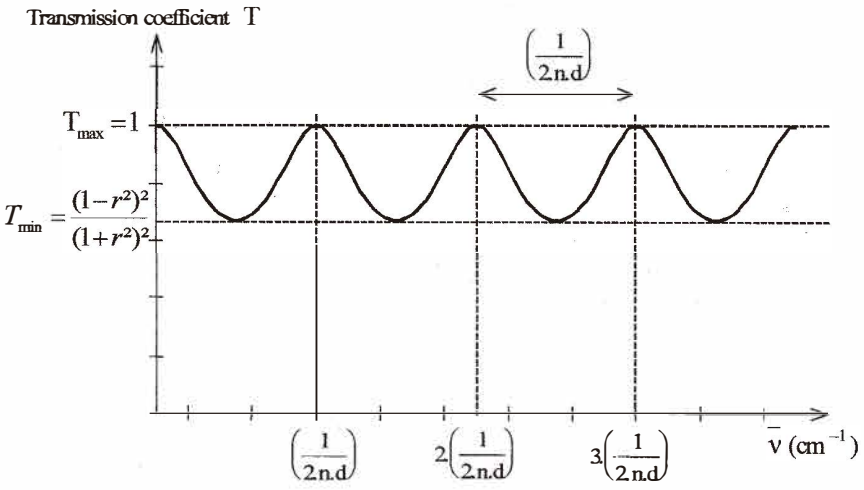

Fig. 2. Coefficient of transmission vs the wave number for a transparent material (t=1).

or $$A(\lambda) = \tau^2 - T(\lambda). \quad (10)$$

The transmission coefficient τ at the interface given by eq. (3) is supposed to be constant inside the spectral band considered. The transmission spectrum $T(\lambda)$ is given directly by an IR spectrometer and the spectral absorptivity $A(\lambda)$ for a membrane of predetermined thickness can be deduced using eq. (10).

The extinction coefficient $k(\lambda)$, which characterizes the properties of the bulk material, is obtained by solving eq. (8). For membranes of any thickness d, the absorption coefficient $A(\lambda)$ is determined by eq. (9).

3. Preparation and Technological Realization of the Polyimide Membranes

Distributed by ULTRADEL™,[7] the different polyimides studied were numbered 3112, 4208 and 4212 and have the same chemical composition; only the concentration of the solvents is varied to control the thickness of the resulting layer.

The solvents are evaporated during polymerization curing; consequently these polyimides have identical transmission spectra.

The (100) GaAs wafers are well adapted for membrane fabrication because they can be completely recessed by acid solutions without damage to the polyimide.[8]

The polyimide layer is very easily deposited by spin coating and high thickness ranging from 0.5 μm to 25 μm can be obtained by successive steps. Areas of membranes must be greater than the dimension of the IR beam (about cm^2) to avoid diffraction at the edges.

The usual GaAs etching solution consists of de-ionized water, hydrogen peroxide (H_2O_2), which is an oxidizing component, and sulfuric acid (H_2SO_4) which dissolves the oxide by removing arsenide and gallium atoms. The patterned samples are vertically dipped in 1:8:1 H_2SO_4:H_2O_2:H_2O for 30 min at room temperature without agitation of the etch bath. The etch rate is 15 μm/min.

Because of the very weak mechanical residual stress in this polymeric material, the manufacturing efficiency of the membranes is excellent. A photograph of a realized membrane is shown in Fig. 3.

4. Results of the Spectral Characterizations of the Membranes

For a 5-μm-thick 4212 polyimide membrane, the transmission spectrum was measured from 10 000 to 370 cm^{-1} by IR spectrometry (Fig. 4). Two regions can be easily distinguished. In the region from 10000 to 2000 cm^{-1}, absorption is very weak and the undulations are typical of multiple reflections.

In the region from 2000 to 370 cm^{-1}, strong absorption peaks appear at the same frequencies for all polyimides considered as shown in Fig. 5.

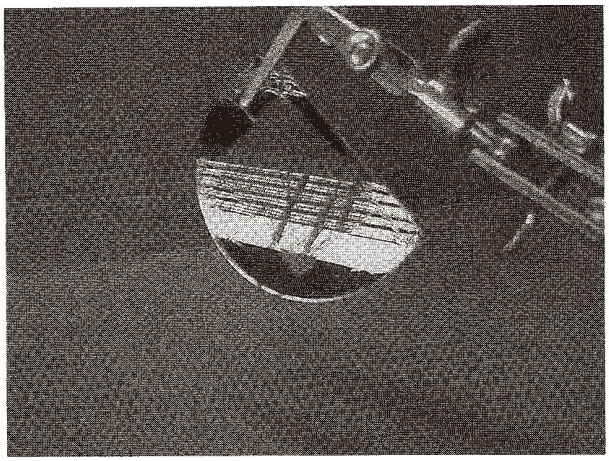

Fig. 3. Photograph of a polyimide membrane realized on a GaAs wafer.

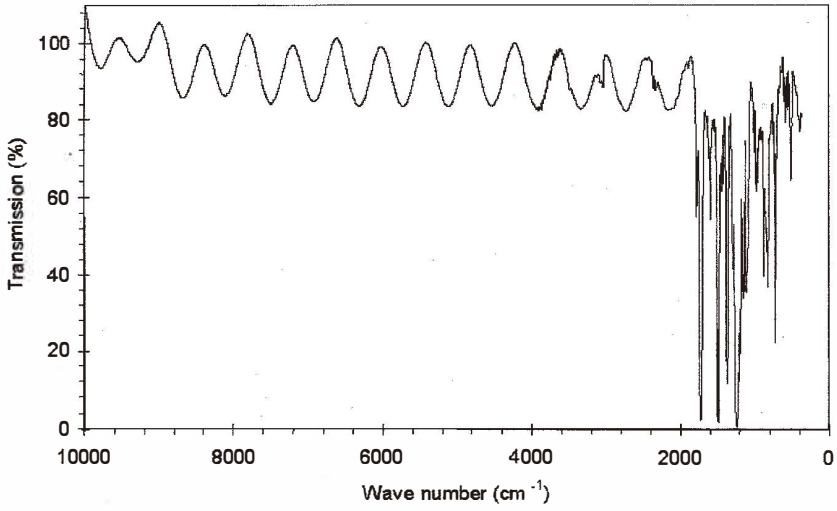

Fig. 4. Transmission spectrum of 4212 polyimide membrane (thickness 5 μm).

4.1 *Determination of the amplitude reflection coefficients r in the region from 10000 to 2000 cm^{-1}*

In this wavelength region of weak absorption, the reflection coefficient r of each material can be deduced from the minimal values of the transmission coefficients (T_{min}) measured for the various membranes (eq. (6)).

In the same way, the index of refraction can be calculated ($n= (1+r)/(1-r)$) and compared with the values given by the manufacturer. These data are listed in Table 1.

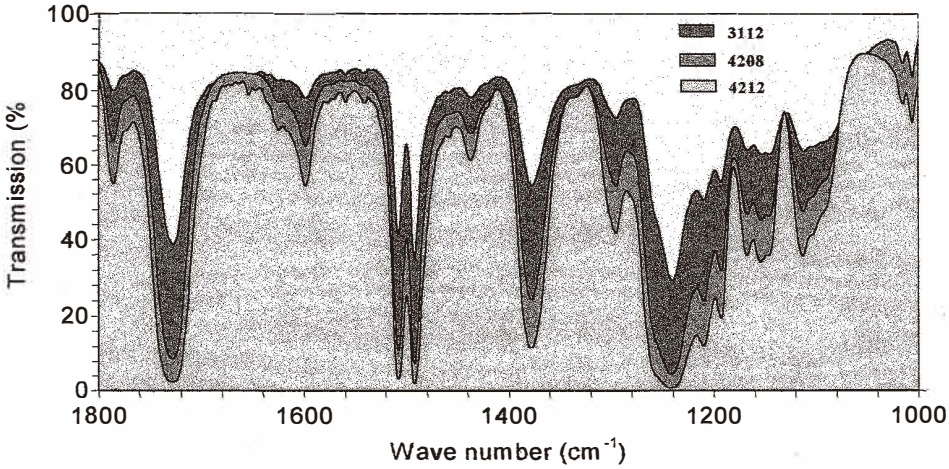

Fig. 5. Transmission spectra of 3112, 4208 and 4212 polyimide membranes with thicknesses of 1.2 μm, 3.3 μm and 5 μm, respectively.

Table 1
Experimental polyimide coefficients from IR.

Polyimide number	Minimal transmission coefficient (T_{min})	Reflection coefficient (r)	Refraction index (n)	Refraction index (manufacturing data)
3112	0.823	0.220	1.57	1.62
4208	0.825	0.219	1.56	1.62
4212	0.827	0.218	1.56	1.62

To obtain a correct value of the absorptivity, a precise measurement of the reflection coefficient is needed. Relative differences between the measured refractive indexes and manufacturing data[7] of less than 4% have been obtained. This result gives an indication of the good precision achievable with absorptivity measurements.

4.2 *Determination of the absorptivity A(λ) in the region from 2000 to 370 cm^{-1}*

Each polyimide is characterized by transmission IR for at least three different membrane thicknesses. As an example, the spectral transmission coefficients for various thicknesses of 3112 polyimide are represented in Fig. 6.

From these transmission spectra T(λ) and from the values of the reflection coefficient r (Table 1), the corresponding absorption coefficients A(λ), represented in Fig. 7, can be deduced using eqs. (3) and (10).

The sensitivity of the microradiometer is known to be proportional to the absorptivity.[4] For any membrane thickness the determination of the extinction coefficient k(λ)

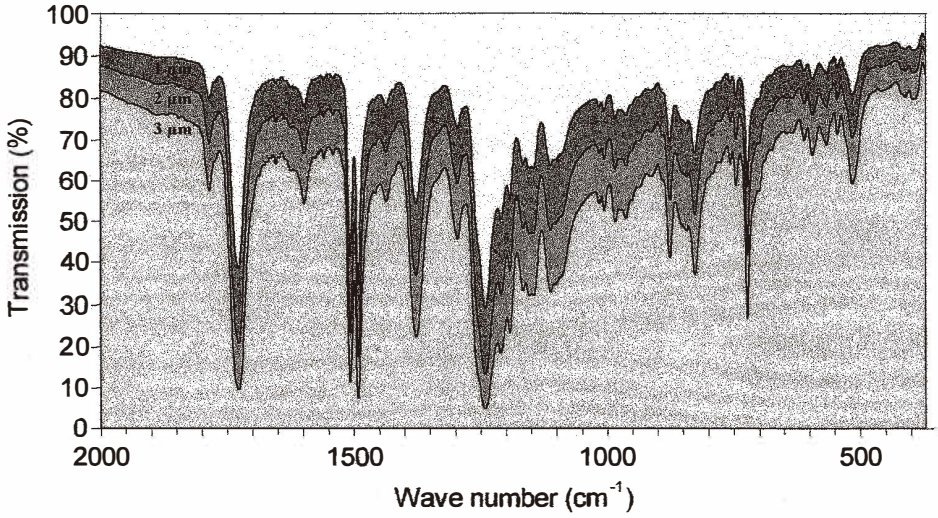

Fig. 6. Transmission spectrum of 3112 polyimide for 1, 2 and 3 μm thicknesses.

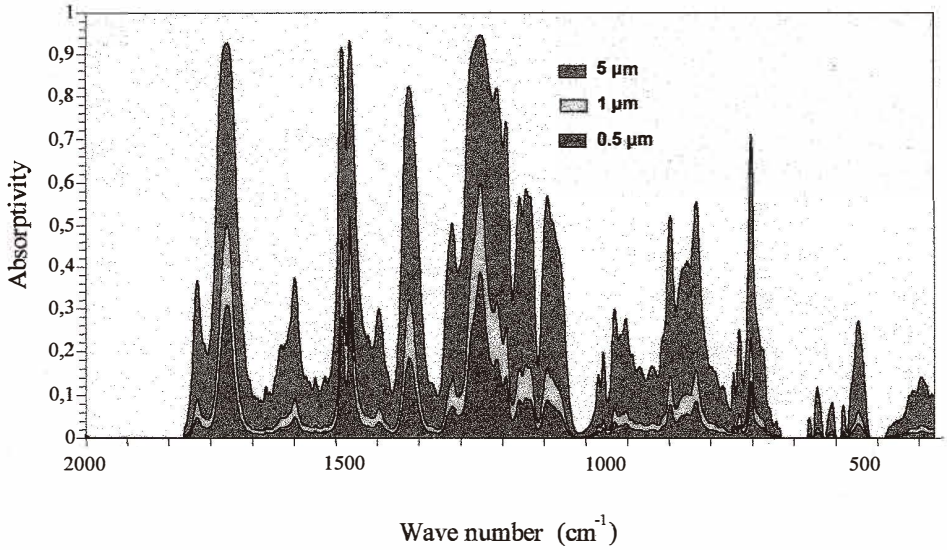

Fig. 7. Spectral absorptivity of the 3112 polyimide for 0.5 μm, 1 μm and 5 μm thicknesses.

allows the absorptivity $A(\lambda)$ (eq. (9)) and then the sensor spectral sensitivity to be calculated.

Furthermore, to evaluate and easily compare the properties of various coatings, the average value of the absorptivity coefficient can be computed by integrating the wave-

length range considered. The average absorptivity of polyimides in the range 2000-370 cm^{-1} vs the membrane thickness is shown in Fig. 8.

Other membranes were produced and the corresponding average absorptivities are represented by the solid circles on the curve. These last points and the calculated curve agree with an error lower than 5%.

5. Conclusions

The benefit of using polyimide as an absorbing layer for radiation microsensors has been demonstrated.

For a deposited thickness of one micron, the average absorptivity of silicon nitride or oxide is very close to polyimide (0.1) but the absorption bands are not located at the same wavelengths. However, polyimide layers can be advantageously deposited in thicknesses greater than SiO_2 or Si_3N_4 films (typically < 2 μm).

The absorptivity of a 10-μm-thick polyimide coating reaches 0.375 and, when used on a microradiometer, the part of the radiation absorbed is increased to 0.5. Such an improvement is obtained because the layer is traversed twice by the radiation which is reflected by the wafer. All occurs as if the thickness of the layer were doubled, i.e., as if it was 20 μm.

Furthermore, a simple method allowing measurement of absorption spectra of a polyimide resist using a typical spectrometer has been validated.

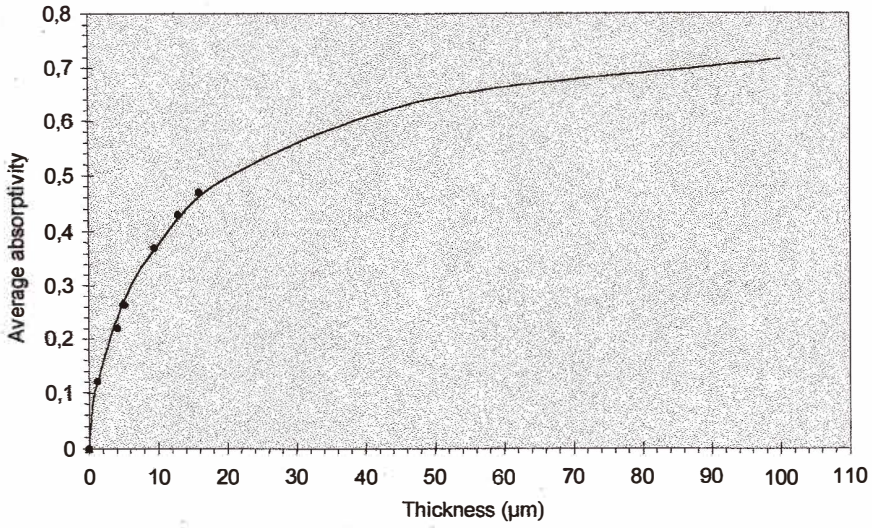

Fig. 8. Average absorptivity of 3112, 4208 and 4212 polyimides vs thickness. The solid circles correspond to various realized membranes.

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