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# Optical properties of AlN/$SiO_2$ nanocomposite layers♣

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AlN is a III-V compound that has attracted interest because of its applications in optoelectronics, high temperature electronics and anti-wear coatings. In recent years, a trend of significant importance has been the synthesis of AlN nanostructured thin films. In this study, AlN nanoclusters are formed in amorphous thermal $SiO_2$ on Si substrates, by sequential implantation of Al and N ions. As an implantation technique, plasma ion immersion implantation (PIII) is used. Infra-red (IR) transmission spectra (500-1200 $cm^{-1}$) of the $SiO_2$ films containing crystalline AlN nanoparticles (NP) on Si substrates are simulated. Firstly the dielectric permeability of the nanocomposite is calculated by means of Bruggeman's effective medium theory (EMT) or a homogeneous mixture of spheres (AlN and $SiO_2$). The nanoparticles' filling factor is estimated by elastic recoil detection analysis (ERDA). Then, the IR transmission spectra of the structure containing two layers (film and substrate) are calculated, taking into account multiple internal light reflections. The results are compared with experimental IR optical transmission spectra. A very good correspondence between theory and experiment is found when the influence of the nanosize effect on the vibrational properties is assumed.

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## 1. Introduction

Nanocomposites consisting of AlN nanoparticles embedded in $SiO_2$ have generated much interest in microelectronics and optoelectronics, because of the strong quantum confinement of electrons and holes.

An understanding of the dielectric properties of Si/$SiO_2$-AlN nanocomposite materials is necessary for interpreting the experimental results of infra-red (IR) transmission, as well as for obtaining additional information for the composite layers, e.g. their transport properties and the size-induced changes in the dielectric permittivity of the nanoparticles. However, this problem is not trivial, because the properties of a nanocomposite material depend on the individual properties of the system components (particles and matrix), as well as on the dipole-dipole interaction between them. This problem is usually approached with the effective medium approximation, where an effective medium having the same dielectric response as the composite material is considered.

The present paper is concerned with modelling the permittivity and IR (500-1200$cm^{-1}$) transmission of Si/$SiO_2$-AlN nanocomposites. The dielectric permeability of the nanocomposite is calculated in the framework of Bruggeman's effective medium theory (EMT) [1]. The IR transmission spectra are simulated taking into account the real film and substrate structure of the samples. The IR transmission results are compared with experimental IR transmission spectra measured in such nanocomposite samples and a discussion is given about the correspondence between theory and experiment. The AlN nanoclusters are formed by implantation of aluminum and nitrogen ions in amorphous thermal $SiO_2$ on a Si substrate. As an implantation technique, plasma ion immersion implantation (PIII) is considered.

## 2. Calculation of the dielectric permittivity in the effective medium approximation

The effective medium approximation (EMA) is a theoretical method which defines an average dielectric constant $\varepsilon_{eff}(\lambda)$ for the whole system, taking into account the local field acting on a particle, which depends on the polarizations of the other particles. EMA is applicable only for particles much smaller than the wavelength of the incident light. This condition is fulfilled, since the incident light is in the mid infra-red range ($\lambda$ > 6 μm) and the average size of the AlN particles should be in the nanometer scale.

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Various versions of EMT exist, but most of them can be applied only for small filling factors of particles in a matrix. The most universal theory, applicable for the whole range of filling factors (0 < f < 1) is given by Bruggeman [1]. It takes into account the dependence of the effective dielectric constant on the microscopic structural geometry of the composite, which is very important for the region of large filling factors when percolation begins to occur. As the filling factor of the experimental samples investigated in the present paper range between 0.25 and 0.30, the universality of Bruggeman's approximation was preferred for the calculations.

According to the Bruggeman model (homogeneous mixture of spherical particles) the effective dielectric constant $\varepsilon_{\text{eff}}$ can be obtained from the equation

$$f\frac{\varepsilon_i-\varepsilon_{\text{eff}}}{\varepsilon_i+2\varepsilon_{\text{eff}}}+(1-f)\frac{\varepsilon_{\text{m}}-\varepsilon_{\text{eff}}}{\varepsilon_{\text{m}}+2\varepsilon_{\text{eff}}}=0 \quad (1)$$

where $\varepsilon_i$ is the dielectric constant of the spherical particles representing the inclusions, $\varepsilon_{\text{m}}$ is the dielectric constant of the spherical particles representing the matrix and $f$ is the filling factor of the inclusions in the sample.

We consider a nanocomposite layer consisting of crystalline spherical AlN inclusions embedded in an amorphous $SiO_2$ matrix. The spectral dependence of the real $n$ and imaginary $k$ parts of the complex refractive index for $SiO_2$ and AlN are taken from [2, 3], respectively. Linear interpolation is applied in order to obtain data with a constant step of the wave number (1 $cm^{-1}$). From the values of $n$ and $k$, the real $\varepsilon_1$ and imaginary $\varepsilon_2$ parts of the corresponding dielectric permittivity are computed. The results are used to calculate $\varepsilon_{\text{eff}}$. Equation (1) is quadratic with respect to $\varepsilon_{\text{eff}}$. The dielectric constants are complex numbers, so that in practice it is required to make a selection of the proper branch from the corresponding multi-valued complex inverse power function, in order to obtain the correct dielectric constant [4]. The approach developed by Roussel et al. [4] consists of transformation of the equations in a reduced form, leading to a radicand formulation that yields the correct value of the proper branch of the complex inverse power function involved.

To solve Eq. (1), we have used both Roussel's approach and the straightforward solution:

$$\varepsilon_{\text{eff}}=\frac{-3f\varepsilon_{\text{m}}+3f\varepsilon_i-\varepsilon_i+2\varepsilon_{\text{m}}\pm\sqrt{(3f\varepsilon_{\text{m}}-3f\varepsilon_i+\varepsilon_i-2\varepsilon_{\text{m}})^2+8\varepsilon_{\text{m}}\varepsilon_i}}{4} \quad (2)$$

choosing the root with "+", because the second root with "–" returns negative values for the $\varepsilon_{\text{eff}}$ imaginary part, which have no physical meaning. In both cases, we have obtained the same results for the spectral dependence of $\varepsilon_{\text{eff}}$. We have verified that indeed Roussel's approach always rejects the roots without physical meaning, and returns the proper one.

In the calculations of the transmission spectra, we employ the LQR method [5] which allows consideration of the real structure, consisting of the crystalline Si substrate and the $SiO_2$-AlN nanocomposite film. The LQR method is developed for a multiple-layers structure, and takes into account the multiple internal light reflections. The input parameters are the thickness and the complex refractive index of each layer of the structure [5].

The calculations are performed in the range 500 to 1200 $cm^{-1}$ for various values of the filling factor $f$ of the AlN inclusions in the $SiO_2$ matrix, ranging from $f$ = 0 (pure $SiO_2$) to $f$ = 0.32. For this purpose a computer program, based on Bruggeman's method and Roussel's approach is elaborated. The nanoparticle filling factor is estimated by means of elastic recoil detection analysis (ERDA).

### 3. Experimental samples

Beside the ability to implant large areas simultaneously, PIII is a very attractive method for obtaining broad profiles within one implantation, due to the energy spread and the presence of multiple ions in the plasma. Aluminium and nitrogen have been implanted simultaneously into layers of amorphous thermal silica ($SiO_2$), in an attempt to bond Al with N and form the binary compound AlN. The $SiO_2$ oxide thickness was 50 nm. PIII was performed in a UHV system equipped with a 40.68 MHz RF plasma source and a cathodic arc, to produce the Al ions. The acceleration voltage was 10 kV, hence kinetic energies between 2.5 and 10 keV were obtained for $N^+$ and $N_2^+$ ions, while 5 to 30 keV were obtained for $Al^+$, $Al^{2+}$ and $Al^{3+}$ ions, contained in the plasma. The high voltage pulses had a repetition rate of 3 kHz at a pulse length of 15 μs. Allowing for the different ion masses present in the plasma, a considerable overlap of the implanted profiles could be expected. In this way, the implanted atoms are distributed from the surface down to about 50 nm, assuming that surface sputtering is negligible.

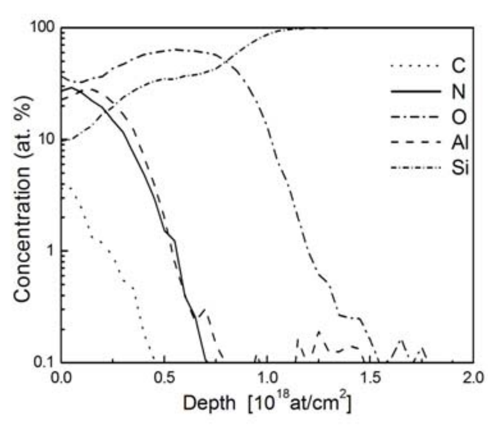


*Fig. 1. Depth distribution of elements from ERDA analysis. The nanocomposite is produced by parallel N and Al PIII at 10 kV.*

The incident ion fluencies were varied from $8\times10^{16}$ to $5\times10^{17}$ Al and N atoms/cm$^2$. The resulting concentrations were predicted by SRIM simulations to be around 25 – 30 at.%, still favoring the formation of stoichiometric AlN nanocrystals while avoiding the formation of a closed buried AlN layer. We should note that although the temperature is not intentionally increased, the ion collisions raise the local temperature of the matrix, but this does not exceed 100ºC. The nanoparticle filling factor *f* has been estimated by measuring the depth profiles of the atomic concentrations of Al and N by means of ERDA (Fig.1). The two concentrations are nearly equal, and varying between 20 and 30 at.% at the plateau of the distributions.

IR spectra were measured in transmission mode, using a UR 20 spectrometer with a resolution of 2 cm$^{-1}$.

## 4. Results and discussion

Fig. 2 displays the measured and calculated IR transmission spectra. The absorption features around 450 and 1100 cm$^{-1}$, related to the rocking, bending and stretching absorption modes of the Si-O-Si units, are clearly seen in all the spectra. The dip at 610 cm$^{-1}$ is due to the Si-Si bonds from the substrate. Features appearing in the range 650-850 cm$^{-1}$ gain intensity with increasing filling factor *f*, which allows us to suppose that they are manifestations of the AlN nanoparticles.

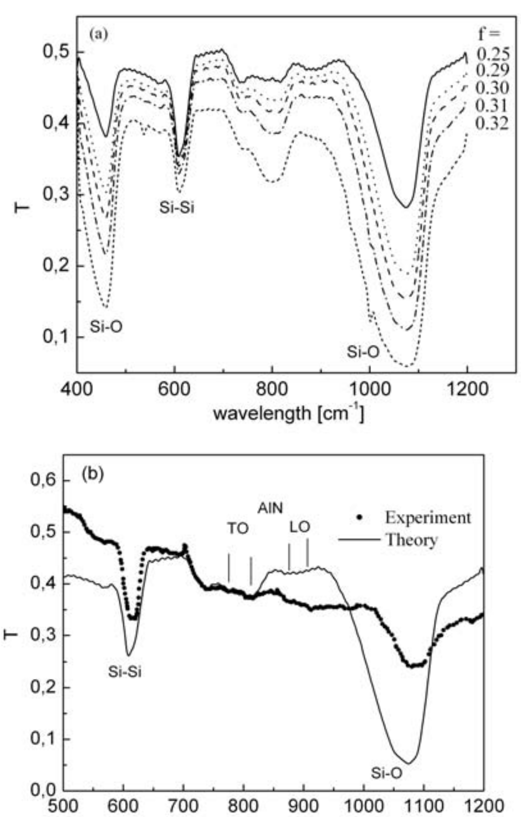


*Fig. 2. (a) Simulated IR transmission spectra of a nanocomposite Si/SiO$_2$-AlN sample, filling factor f=25;29;30;31;32;(b)experimental IR transmission spectrum compared with a simulated one for f=0.29. Modes from the Si substrate (610 cm$^{-1}$), from SiO$_2$ (450, 1100 cm$^{-1}$) and in the range of the LO and TO modes of AlN are marked.*

The most pronounced and IR sensitive features in the transmission of bulk AlN are the transverse optical (TO) mode at 660-670 cm$^{-1}$ and the longitudinal optical (LO) mode at 880-915 cm$^{-1}$ [6]. However, fornanoscale AlN crystals when quantum size effects become pronounced, a broad band at 750 cm$^{-1}$ was observed for cubic AlN nanoparticles [7], while for wurtzite nanoparticles embedded in different matrices [8], broad peaks centered at about 770 cm$^{-1}$ and 800 cm$^{-1}$ and a sharp peak at about 660 cm$^{-1}$ were obtained.

The experimental spectrum shows increased free carrier absorption due to the high carrier concentration in the Si substrate, which is not taken into account in the calculations. Nevertheless, very good correspondence is found for the sample with *f*=0.29 between the calculated and experimental curves in the spectral range from 700 to 900 cm$^{-1}$, where AlN vibration mode features appear. Thus the importance of taking into account the real film and substrate structure in simulating the IR properties of nanocomposites is demonstrated.

## 5. Conclusions

The dielectric properties and the IR transmission spectra of SiO$_2$ films containing crystalline AlN nanoparticles on Si substrates have been simulated. The dielectric permittivity of the nanocomposite is calculated in the framework of Bruggeman's effective medium theory. The IR transmission spectra are calculated by means of the LQR method, taking into account the real film and substrate structures. The comparison with experimental IR transmission spectra measured in SiO$_2$-AlN nanocomposite samples has shown a very good correspondence and the manifestation of a nanosize effect in the dielectric properties. This study highlights the importance of taking into account the real film and substrate structure in simulating the IR properties of nanocomposites. Further simulations of the IR transmission spectra can help us to refine the information about the dielectric constant of the nanocomposite, as well as to explore surface modes in the AlN nanoparticles and size-induced changes of their dielectric constants.

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