

STRUCTURE AND OPTICAL PROPERTIES OF $\text{Si}_3\text{N}_4/\text{Ag}/\text{Si}_3\text{N}_4$ AND $\text{BN}/\text{Ag}/\text{BN}$ TRILAYERS: A COMPARATIVE STUDY

J. Toudert, S. Camelio, D. Babonneau and T. Girardeau

Laboratoire de Métallurgie Physique, UMR CNRS 6630 – Université de Poitiers, SP2MI,
Boulevard M. et P. Curie, 86962 Futuroscope Chasseneuil Cedex, France

Received: May 4, 2005

Abstract. Nanocomposite $\text{BN}/\text{Ag}/\text{BN}$ and $\text{Si}_3\text{N}_4/\text{Ag}/\text{Si}_3\text{N}_4$ trilayers containing a similar amount of silver have been synthesized by alternate ion beam sputtering of the metal and dielectric species. Their optical transmittance spectra at oblique incidence for a p-polarized light present two surface plasmon resonance (SPR) bands which positions can be interpreted using the generalized Maxwell-Garnett model. It suggests that both trilayers contain oblate ellipsoidal metal clusters, with a flatter shape in the case of $\text{Si}_3\text{N}_4/\text{Ag}/\text{Si}_3\text{N}_4$, in qualitative agreement with the structural informations obtained from cross-section transmission electron microscopy (TEM) characterization. The average height to lateral size ratio of the truncated ellipsoidal clusters observed by this technique is close to 1 (respectively 0.7) when they are embedded in a BN (respectively Si_3N_4) matrix. Consequently, the nature of the matrix plays a key role in determining clusters shape, which then influences the position of the SPRs.

1. INTRODUCTION

Composite materials constituted by noble metal nanoclusters embedded in a ceramic matrix (nanocermet) exhibit a strong absorption band [1] and a high non-linear third-order susceptibility [2] at the surface plasmon resonance (SPR), which make them potential candidates for technological applications such as optical filters and ultrafast optical switches. The SPR phenomenon occurs when the conduction electrons of the metal nanoclusters are excited by an electromagnetic wave at the SPR wavelengths of the nanoclusters. These wavelengths – usually located in the visible range – are known to depend on the nature of the metal [1] and the matrix [3], on clusters size [1,4], on their repartition into the matrix [5], and on their shape [1,5,6]. It is therefore useful to control these

parameters, in order to synthesize materials with an adjustable SPR spectral position.

As shown in previous papers [7,8] in the case of nanocermet thin films elaborated by ion beam sputtering, it is possible to tailor the shape of the nanoclusters by adjusting the elaboration parameters, and consequently to control the position of the SPR absorption band (s): the codeposition of the metal and the dielectric leads to the formation of ellipsoidal clusters elongated in the growth direction of the film (prolate shape), while flatter truncated ellipsoidal clusters (oblate shape) are obtained in the case of alternate sputtering of the metal and the matrix. In the latter case, a control of the height to lateral size ratio of the clusters is then achieved by varying the amount of deposited metal. In these studies, it has been shown that a single SPR is ob-

Corresponding author: J. Toudert, e-mail: johann.toudert@etu.univ-poitiers.fr

served at normal incidence, whereas a second resonance appears at oblique incidence for a p-polarized light if the clusters display anisotropic shapes. The spectral position of these SPRs shifts with changes of the average height to lateral size ratio of the clusters.

An alternative way to influence the spectral position of this (these) SPR band (s) by changing the nature of the dielectric matrix is investigated here. For this purpose, a $\text{Si}_3\text{N}_4/\text{Ag}/\text{Si}_3\text{N}_4$ and a $\text{BN}/\text{Ag}/\text{BN}$ trilayer have been elaborated by alternate ion beam sputtering deposition of the dielectric and metal species. The aim of this paper is to present the correlation between the nature of the dielectric material, the topology of the trilayers – investigated by TEM – and their optical transmittance spectra.

2. EXPERIMENTAL DETAILS

A sputtering beam of 1.2 keV argon ions was used to sputter alternatively a Si_3N_4 (resp. BN) dielectric target and a silver target, in order to obtain a $\text{Si}_3\text{N}_4/\text{Ag}/\text{Si}_3\text{N}_4$ (resp. $\text{BN}/\text{Ag}/\text{BN}$) trilayer. The sputtered target and the heating substrate holder were facing each other. In order to obtain the good stoichiometry for the dielectric species, the substrates were heated at 200 °C and irradiated with a 50 eV nitrogen ion beam (assistance beam) during the deposition of the dielectric. The energy of the assistance beam was decreased to 5 eV during the deposition of the metal. The deposition times were adjusted in order to obtain effective thicknesses around 15 nm for the dielectric species and 1.5 nm for silver. The films were deposited on fused silica (for optical transmittance measurements), carbon-coated grids and silicon substrates (for plane-view and cross-section TEM analysis respectively).

The optical transmittance spectra of the films were measured at normal (0°) and oblique incidence (65°), using the p-polarized light of a xenon lamp. The wavelength ranged from 210 nm to 900 nm with a 10 nm monochromator step. TEM characterization was performed with a JEOL 200 CX electron microscope, operating at a 200 kV voltage.

3. RESULTS AND DISCUSSION

Fig. 1 regroups the transmittance spectra obtained for both trilayers at normal (Fig. 1a) and oblique (Fig. 1b) incidence. At normal incidence, one strong absorption band can be seen whatever the nature of the dielectric. It is located at a shorter wavelength in the case of the $\text{BN}/\text{Ag}/\text{BN}$ trilayer. At oblique incidence (p-polarization), a second - weak - absorp-

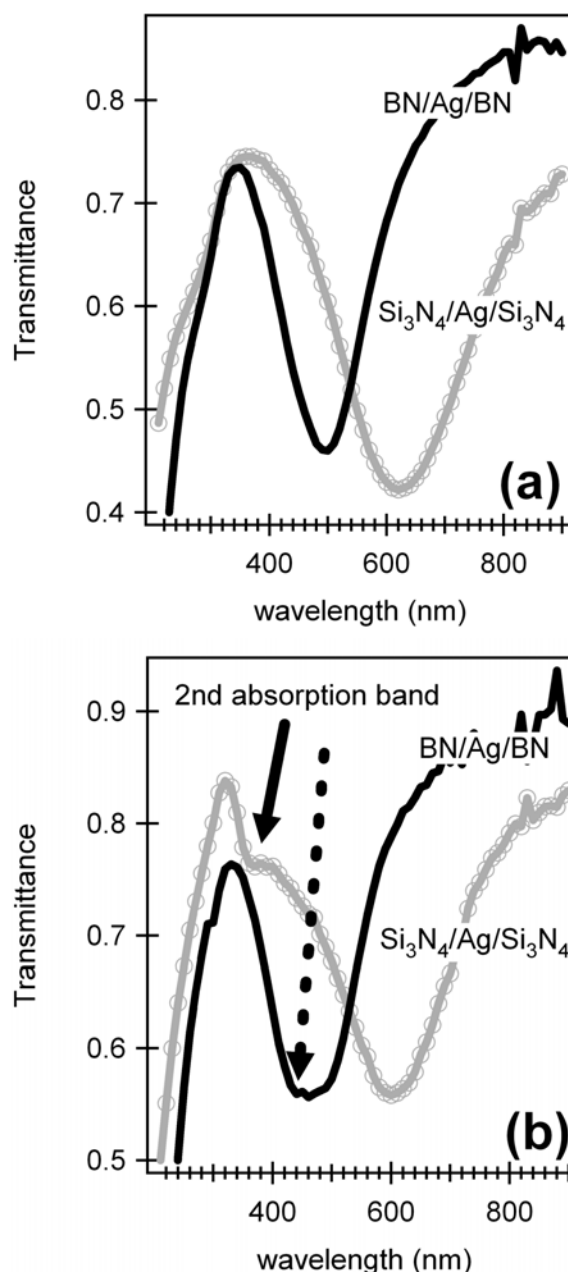


Fig. 1. Optical transmittance spectra of the $\text{Si}_3\text{N}_4/\text{Ag}/\text{Si}_3\text{N}_4$ and $\text{BN}/\text{Ag}/\text{BN}$ trilayers, (a) at normal incidence, (b) at oblique incidence (65°) with a p-polarized light. For the sake of clarity, a slight vertical offset (+0.08) has been applied to the curve corresponding to the $\text{Si}_3\text{N}_4/\text{Ag}/\text{Si}_3\text{N}_4$ trilayer in (b).

tion band appears at a shorter wavelength than the strong absorption band that is still present. The main and the second bands are well separated in the case of the $\text{Si}_3\text{N}_4/\text{Ag}/\text{Si}_3\text{N}_4$ trilayer, and very close one to another in the case of the $\text{BN}/\text{Ag}/\text{BN}$ trilayer. The

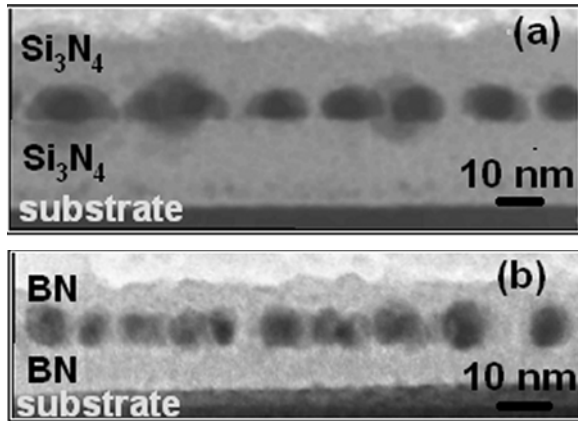


Fig. 2. Examples of cross-section view micrographs of (a) the $\text{Si}_3\text{N}_4/\text{Ag}/\text{Si}_3\text{N}_4$ trilayer, and (b) the $\text{BN}/\text{Ag}/\text{BN}$ trilayer.

spectral position of each absorption band can be found in Table 1.

The absorption bands observed here can be attributed to the excitation of surface plasmon resonances of metal clusters. As in the case of the $\text{Si}_3\text{N}_4/\text{Ag}/\text{Si}_3\text{N}_4$ trilayers studied in the past [8], let us assume that the clusters are ellipsoids with two in-plane axes (D_x, D_y) of equal length ($D_x = D_y = D_{xy}$) and a revolution axis D_z normal to the interface of the thin film. At normal incidence, the electric field is parallel to the D_{xy} axis. As a consequence, the absorption band observed in this case is due to the excitation of the collective oscillation of the electrons along D_{xy} ((1,1) mode). At oblique incidence for p-polarized light, the electric field is the superposition of two components. The first one is oriented along D_{xy} and is still responsible for the main absorption band. The other one (along D_z) causes a collective oscillation of the electrons along D_z which

is responsible for the second absorption band ((1,0) mode).

Assuming that the nanocermet is constituted by a monodisperse assembly of ellipsoidal clusters with a size ranging between 5 and 25 nm (for which no size effect on the position of the SPRs is expected [1,4]), the generalized Maxwell-Garnett model can be used to extract qualitative informations concerning clusters morphology and environment from the spectral position of the absorption bands [8].

It predicts a shift of both modes towards the same direction when the refractive index of the matrix is varied [3,7]. Here, the (1,1) and (1,0) modes of the $\text{BN}/\text{Ag}/\text{BN}$ trilayer appear respectively at a lower and a higher wavelength than those of the $\text{Si}_3\text{N}_4/\text{Ag}/\text{Si}_3\text{N}_4$ trilayer. This behavior cannot be explained by assuming different values for the refractive index of BN and Si_3N_4 . Moreover, from the values of the refractive index of BN and Si_3N_4 (resp. 1.8 and 2) determined from spectroscopic ellipsometry measurements on pure BN and Si_3N_4 thin films, the position of the two modes should depend only slightly on the nature of the matrix. For example, the presence of silver nanoclusters with a spherical shape is expected to induce a (1,1) mode centered at 490 nm and 510 nm in the case of a BN or a Si_3N_4 matrix respectively.

In the framework of the generalized Maxwell-Garnett model, the other parameter that plays a key role in the spectral position of the two modes is clusters height to lateral size ratio D_z/D_{xy} [8]. For spherical clusters, both modes are expected to occur at the same wavelength and a single resonance can be seen even at oblique incidence for a p-polarized light. In the case of non-spherical shapes, the (1,1) and (1,0) modes are expected to appear at different spectral positions. In the case of prolate (respectively oblate) clusters – i.e. with $D_{xy} < D_z$ (resp. $D_z < D_{xy}$) – the (1,1) mode is blue-shifted (resp.

Table 1. Spectral position of the main absorption band (at normal incidence) and the second absorption band that appears at oblique incidence.

	Main absorption band ((1,1) mode) spectral position at normal incidence (nm)	Second absorption band ((1,0) mode) spectral position (nm)
$\text{Si}_3\text{N}_4/\text{Ag}/\text{Si}_3\text{N}_4$	620	370
$\text{BN}/\text{Ag}/\text{BN}$	498	439

red-shifted) and the (1,0) mode is red-shifted (resp. blue-shifted) compared to the position for spherical clusters. The more the clusters are elongated, the more both modes shift away from the position for spherical clusters. As a consequence, an increase of clusters anisotropy induces an increase of the gap between the position of the two modes. In the present study, whatever the matrix, the (1,0) mode is located at a lower wavelength than the (1,1) mode, suggesting the presence of oblate clusters. Moreover, a higher gap between the spectral position of both modes is observed in the case of the $\text{Si}_3\text{N}_4/\text{Ag}/\text{Si}_3\text{N}_4$ trilayer compared to the case of the $\text{BN}/\text{Ag}/\text{BN}$ trilayer which (1,0) and (1,1) modes can hardly be distinguished. It suggests that the clusters embedded in Si_3N_4 are flatter than those embedded in BN.

These predictions can be compared with observations from cross-section TEM micrographs of both trilayers shown in Fig. 2. Nanoclusters sandwiched between two dielectric layers can be noticed for both trilayers. These clusters – which have already been characterized by plane-view TEM [8] in the case of $\text{Si}_3\text{N}_4/\text{Ag}/\text{Si}_3\text{N}_4$ trilayers – result from a Vollmer-Weber growth of the silver layer on the dielectric buffer. They can be roughly described as truncated ellipsoids which average height/lateral size ratio $\langle D_z/D_{xy} \rangle$ can be estimated from the cross-section view micrographs. One obtains around 1 for the $\text{BN}/\text{Ag}/\text{BN}$ trilayer whereas flatter clusters (with $\langle D_z/D_{xy} \rangle \approx 0.7$) are observed for the $\text{Si}_3\text{N}_4/\text{Ag}/\text{Si}_3\text{N}_4$ trilayer. These results are in qualitative agreement with the morphological informations extracted from the transmittance spectra. The nature of the matrix influences clusters shape, and seems therefore to play a noticeable role in the determination of the spectral position of the SPR bands of the composite material.

An extensive discussion of this ‘matrix effect’ on the shape of the embedded clusters is beyond the scope of this paper. However, a first explanation to this effect can be proposed here. Si_3N_4 is known to be amorphous in the present experimental conditions [8]. As a consequence, in the case of clusters embedded in Si_3N_4 , the cluster/matrix interface energy is expected to be the same everywhere at the cluster surface. On the contrary, in the case of $\text{BN}/\text{Ag}/\text{BN}$ trilayers, it can be seen that the BN buffer layer under the clusters is constituted by h-BN with (002) planes being oriented along the substrate surface. The top face of the clusters are surrounded by graphene shells [9]. Then, assuming that the interface energy between these shells and the top face

of the clusters is lower than between the bottom face of the clusters and the buffer layer, the most stable shape for the clusters embedded in BN is the one which minimizes the ratio bottom face area/top face area. From this point of view, the most stable shape would present a higher height to lateral size ratio than in the case of an amorphous matrix, as it is effectively observed.

4. CONCLUSION

In the case of trilayers elaborated by alternate ion beam sputtering deposition of silver and a dielectric specy (BN or Si_3N_4), it has been shown that changing the nature of the matrix embedding the nanoclusters induces changes of their morphology. The clusters are flatter when they are embedded in a Si_3N_4 matrix than in a BN matrix. Even if an explanation of this ‘matrix’ effect on clusters shape has been proposed here, further investigations concerning the growth mechanism of the nanoclusters are necessary to determine the key parameters that determine their shape.

On the basis of the generalized Maxwell-Garnett model, qualitative informations on clusters morphology can be extracted from the spectral position of the (1,0) and (1,1) SPR modes. A qualitative agreement with the cluster morphology as determined by cross-section TEM is found. It suggests once more that clusters shape, which is influenced here by the nature of the matrix, plays a noticeable role in the determination of the spectral positions of the SPRs.

REFERENCES

- [1] U. Kreibig and M. Vollmer, *Optical properties of metal clusters* (Springer, Berlin, 1995).
- [2] S. Debrus, J. Lafait, M. May, N. Pinçon, D. Prot, C. Sella and J. Venturini // *J.Appl.Phys.* **88** (2000) 4469.
- [3] A. Hilger, M. Tenfelde and U. Kreibig // *Appl. Phys. B* **73** (2001) 361.
- [4] D. Dalacu and L. Martinu // *J. Appl. Phys.* **87** (2000) 228.
- [5] J. Gonzalo, R.Serna, J. Solis, D. Babonneau and C.N. Afonso // *J. Phys : Cond. Matt.* **15** (2003) 3001.
- [6] S.W. Kennerly, J.W. Little, R.J. Warmack and T.L. Ferrell // *Phys. Rev. B* **29** (1984) 2926.
- [7] S. Camelio, D. Babonneau, T. Girardeau, J. Toudert, F. Lignou, M.-F. Denanot, N. Maître, A. Barranco and Ph. Guérin // *Appl. Opt.* **42** (2002) 674.

[8] S. Camelio, J. Toudert, D. Babonneau and T. Girardeau // *Appl. Phys. B* **80** (2004) 89.

[9] J. Toudert, S. Camelio, D. Babonneau, M.-F. Denanot, T. Girardeau, J.P. Espiños, F. Yubero and A.R. Gonzalez-Elipe, in preparation .