

Viviane Lilian Soethe*
 Technological Institute of Aeronautics
 São José dos Campos/SP – Brazil
 vivianes@reitoria.ufsc.br

Evandro Luis Nohara
 University of Taubaté
 Taubaté/SP – Brazil
 evandro.nohara@unitau.br

Luis César Fontana
 University of Santa Catarina State
 Joinville/SC – Brazil
 fontana@udesc.br

Mirabel Cerqueira Rezende
 Institute of Aeronautics and Space
 São José dos Campos/SP – Brazil
 mirabelmcr@iae.cta.br

*author for correspondence

Radar absorbing materials based on titanium thin film obtained by sputtering technique

Abstract: Titanium thin films with nanometer thicknesses were deposited on polyethylene terephthalate (PET) substrate using the triode magnetron sputtering technique. It was observed that the titanium thin film-polymeric substrate set attenuates the energy of the incident electromagnetic wave in the frequency range of 8 to 12 GHz. This result allows to consider this set as a radar absorbing material, which may be employed in automobile, telecommunication, aerospace, medical, and electroelectronic areas. Results of the reflectivity show that the attenuation depends on the thin film thickness, as a determining factor. Thin films with 25 to 100 nm thickness values show attenuation of the electromagnetic wave energy from around 20 to 50%. Analyses by Rutherford backscattering spectrometry provided information about the thickness of the thin films studied. Hall effect analyses contributed to better understand the influence of the thin film thickness on the electron mobility and consequently on absorption properties.

Keywords: Radar absorbing material, Magnetron sputtering, Thin film, Titanium.

INTRODUCTION

The technology involving thin film deposition on polymeric substrates is being more widely studied, due to its potential application in different areas. Innovations in industry and academic studies involving thin films uses in microelectronics, optics, solar cells, sensors, and special packing areas are cited (Bregar, 2004; Nie *et al.*, 2007). Recent studies show that nanometer thin films deposited on appropriate substrates present physical characteristics different from the ones presented by the conventional films. For example, Kantal films with thickness from 10 to 200 nm, when used as coating in waveguide internal walls, present efficient performance as electromagnetic radiation absorber – more usually known as radar absorbing materials (RAM), due to the frequency range of application. These films, in the frequency range of 16.3 to 17.5 GHz, present absorption values around 0.8 dB (~17% of attenuation), depending on the coating thickness (Bhat, Datta and Suresh, 1998).

RAM present innumerable applications, as in equipment electromagnetic shielding employed in automotive and aerospace industries and military technology, as well as in electrical and electronic devices and systems for wireless communication (Biscaro, Rezende and Faez, 2008; Bregar, 2004; Folgueras and Rezende, 2007; Hashish, 2002; Nie *et al.*, 2007; Rezende, Silva and Martin, 2000). Considering the complexity of the aeronautical engineering

area, technological advances involving RAM depend on the development of materials to attend a wide range of frequencies, in other words, wavelengths varying from m to mm. In this context, RAM development makes more and more important for the control of electromagnetic wave propagation and its harmful effects on living beings and on the equipment.

RAM are characterized by converting the energy of electromagnetic wave into thermal energy. Such materials are classified in two types, according to their interactions with the electromagnetic wave: materials with dielectric losses, which interact with the wave electric field, and materials with magnetic losses, which interact with the wave magnetic field. Conventional microwave absorbers have thickness values between mm to cm and weight/area varying from 1.0 to 20 kg/m² (Fortunato *et al.*, 2002; Hashish, 2002; Mikhailovsky, 1999; Nie *et al.*, 2007).

The RAM studied in this paper is a metallic thin film with dielectric losses. In this case, when an external electric field is applied, several electric dipoles on the dielectric material (thin film) are formed. These dielectric dipoles are guided by the applied electric field. The interaction between the dipoles and the electric field leads to the formation of aligned dipoles, according to the applied electric field, enabling the material to store potential electric energy (Folgueras and Rezende, 2007).

Metallic thin films deposited on appropriate polymeric substrates present particular physical characteristics if

Received: 17/02/11

Accepted: 25/08/11

compared to their bulk materials. As mentioned in the literature, metals are excellent reflectors of microwaves, since they tend to keep null the electric field on their surfaces (Mayes, 2006). However, some metals and transition metals may behave as absorbers when reduced to nanometer thickness. As previously cited, Kantal films with thicknesses varying from 10 to 200 nm perform effectively as RAM when used as coating on waveguide internal walls (Bhat, Datta and Suresh, 1998). In comparison to conventional RAM, the nanometer films can present similar electromagnetic wave attenuation performance, but they are lighter.

Therefore, thin films are able to interact with the electromagnetic wave, forming electric dipoles. In this particular case, the mechanism of absorption is based on the polarization of the metallic film and losses. Firstly, when the electromagnetic wave reaches the film it becomes polarized by the wave electric field and, consequently, electric current (Eddy currents) is produced due to the induced polarization. After that, the electromagnetic wave energy is changed into heat through the known Joule effect (Balanis, 1989; Nohara, 2003), due to the presence of defects in the crystalline structure of the nanofilm, which confers resistance to the electric current.

Thus, the wave attenuation occurs when the thickness values of the metallic layer are smaller than, or at most similar to, the skin depth (δ) value of the metal (Bhat, Datta and Suresh, 1998; Ishii and Yasaka, 2004). The variation of this parameter (δ) depends on the characteristics of the metallic material used in the film production, mainly its electric conductivity, and also on the incident radiation wavelength that interacts with the film (Ohring, 1991). When the metallic layer thickness is adequate, the resulting electric current becomes confined into the film (Salmon, 1993) and losses occur (Bosman, Lau and Gilgenbach, 2003; 2004; Shubin, *et al.*, 2000).

The skin depth value can be estimated by Eq. 1, which correlates frequency (f), electric conductivity (σ) (inverse of electric resistivity) and the magnetic permeability of the vacuum ($\mu = 4\pi \cdot 10^{-7}$ H/m) (Kaiser, 2004; Serway, 1998). For thin films with thickness around nanometers, the electric resistance is very different from the bulk material. Thus, the skin depth estimation, related to the electric resistivity, is an important parameter to support the thin film preparation.

$$\delta = \frac{1}{\sqrt{\pi f \mu \sigma}} \quad (1)$$

where:

δ : is the skin depth;

f : is the frequency;

μ : is the magnetic permeability of the vacuum ($\mu = 4\pi \cdot 10^{-7}$ H/m), and

σ : is the electric conductivity.

Considering the new tendencies in RAM developments and the academic importance of this subject, the aim of this paper was to study the influence of the thickness and electric properties of titanium thin films on the electromagnetic radiation attenuation in the frequency range from 8 to 12 GHz.

MATERIALS AND METHODS

Titanium film deposition

Titanium thin films were deposited on commercial polyethylene terephthalate (PET) substrates, with 0.1 mm of thickness, using the triode magnetron sputtering (TMS) technique, based on the TMS equipment presented by Fontana and Muzart (1998). The present process differs from the conventional magnetron sputtering, due to the presence of a screen parallel to the target, 2.0 cm from it. This screen is grounded and it improves the confinement of the plasma next to the target, thus providing greater stability and higher rate of ionization. This system makes it possible to work at low gas pressures (2.0 mTorr of argon). As a result, the atoms sputtered interact with the substrate without colliding with the gas atoms of the plasma atmosphere. Figure 1 shows a scheme of this system and Table 1 presents the experimental parameters used in the depositions.

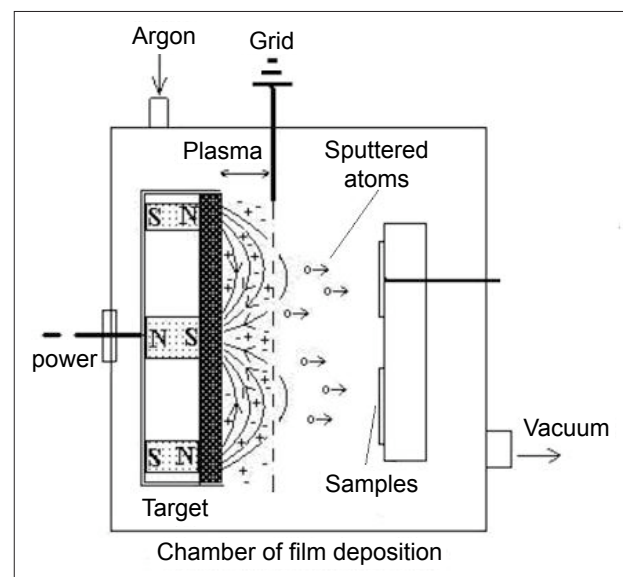


Figure 1. Scheme of the equipment used for the titanium film deposition (based on Fontana and Muzart, 1998).

Table 1. Experimental parameters used for the titanium thin film depositions.

Voltage (V)	Current (A)	Pressure (mTorr)	Time of deposition (s)	Thickness (nm)
-320	2.0	2.0	5-90	25-420

Experimental characterization

Reflectivity measurements were taken in order to obtain the attenuation values of the incident electromagnetic wave in the titanium thin film. These measurements were obtained in a vector network analyzer (8510, Hewlett-Packard, USA). The present experimental apparatus allows evaluating the attenuation value of the metallic thin film stored on the polymeric substrate in the frequency range of 8 to 12 GHz.

The waveguide technique involves a device made with high mechanical precision, where the propagation of electromagnetic wave occurs in a closed system (Nicholson and Ross, 1970). This system basically consists of a waveguide with one terminal to generate the microwave signal and another one to collect the reflected signal that is conducted for spectral analysis (Nohara, 2003). Two different methodologies are used to measure the wave attenuation in this equipment. In the first, it is possible to measure the absorbed energy (E_a) considering the difference between incident (E_i) and transmitted energies (E_t). Figure 2a shows this condition schematically. This setup is similar to the RAM characterization in free space condition and it provides information about the intrinsically energy absorbed. In the second methodology, a metal plate (Al plate) is located behind the thin film/substrate set. In this case, it is evaluated the performance of the sample in the electromagnetic energy attenuation, considering the thin film positioned on the metal plate.

The E_a is obtained by the difference between E_i and the reflected energy (E_r). Figure 2b shows this apparatus schematically. This process simulates the absorber material put on a reflected surface, representing a real situation, for example, the RAM application to aeronautical fuselage. Both methods, schematically presented in Fig. 2, were used to characterize the prepared films.

Surface analyses of the films were performed by the scanning electron microscopy technique (SEM) using an equipment from LEO, model 435 VPI, and thin film samples without special preparation. Rutherford backscattering spectroscopy (RBS) (Bubert *et al.*, 2002) was also employed to complete the surface characterization of the films. For this, a beam of He^+ with energy of 2.2 MeV was used. The results were analysed by the RUMP software (Doolittle, 1985). Based on the SEM and RBS analyses the morphology and the thickness of the films were evaluated, respectively.

The thickness of the films was also evaluated by profilometry technique, using an equipment Dektak 3030, and thin film samples were deposited on silicon plates, simultaneously to the thin film deposition on PET substrate. This methodology guarantees the same thickness for the deposited films on two different substrates. The silicon plate has an adhesive tape that is pull out from the silicon substrate before the profilometry analysis, creating a step between the silicon substrate and the deposited film. This step is measured by a tip moving on the sample.

The electric resistivity of the films was evaluated by a four-point resistivity methodology using an equipment Veeco, model FPP5000. The electronic mobility was measured by the Hall effect technique using a Hall system produced by Bio-Rad Company, model HL5500.

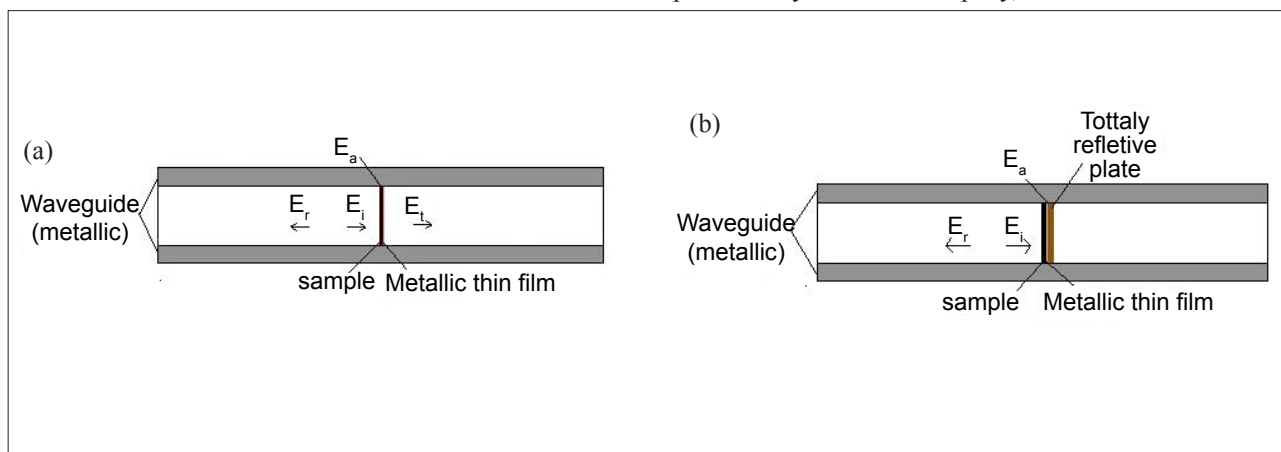


Figure 2. Waveguide settings used for the reflectivity measurements of the titanium films: (a) evaluation of the intrinsic absorption; (b) reflectivity with metallic plate (adapted from Nohara, 2003). E_a : absorbed energy; E_r : reflected energy; E_i : incident energy; E_t : transmitted energy.

RESULTS AND DISCUSSION

The profilometry measurements show that the titanium thin films were deposited at 3.6 nm/s on both polymeric and silicon substrates. This parameter, when determined by RBS analyses, shows values close to 5.0 nm/s. Besides the differences observed, these values present the same magnitude. However, considering that the RBS is a technique more precise, the thin film thickness values were calculated based on the deposition rate of 5.0 nm/s. The RBS analyses also show that the thin films are homogeneous, that is, without impurities. These results are attributed

to the adequate parameters used in the deposition process, how high the deposition rate and low pressure (vacuum) were during the process.

SEM analyses of titanium thin films with 25, 45 and 150 nm of thickness show similar morphologic aspects for the analysed surfaces (Fig. 3). In the used magnification, Fig. 3 shows surfaces with large uniformity, continuous structure, and absence of imperfections.

Figure 4 shows the average of the reflectivity measurements in the frequency range of 8 to 12 GHz

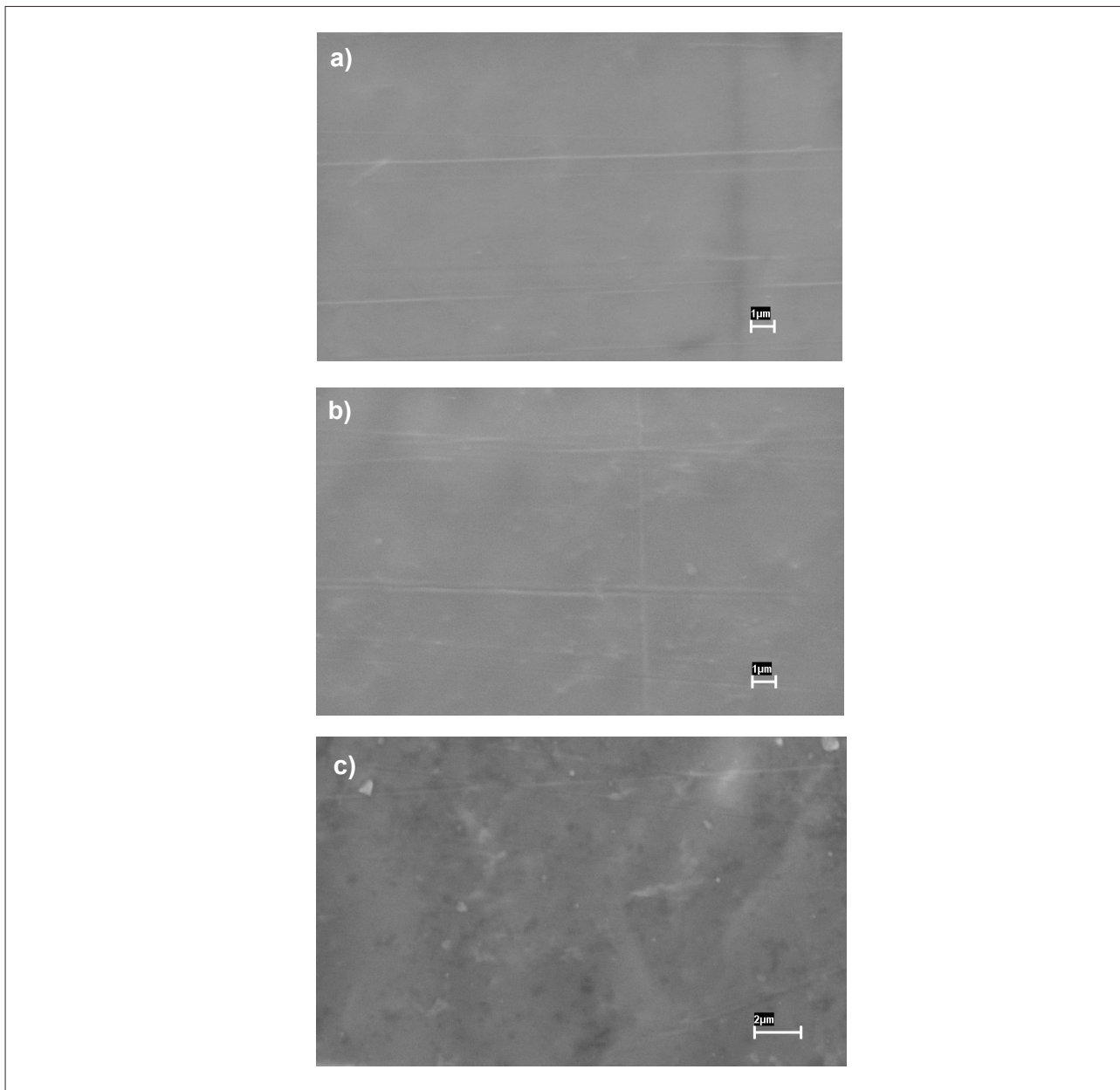


Figure 3. Scanning electron microscopy technique of titanium thin film with different thickness values: (a) 25 nm; (b) 45 nm, and (c) 150 nm.

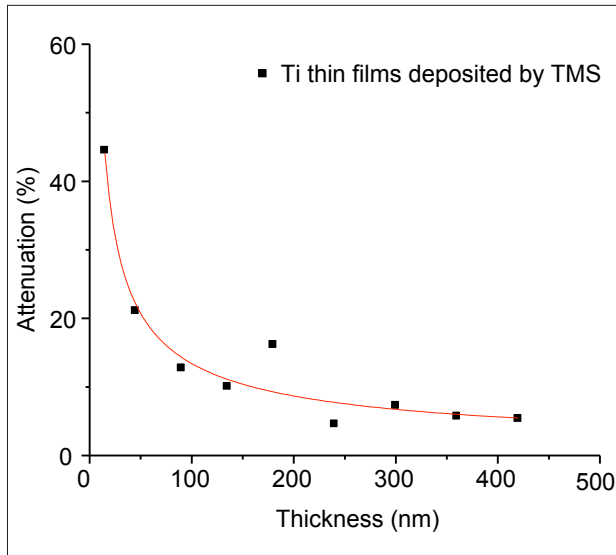


Figure 4. Relationship between microwave attenuation and titanium thin film thickness.

for the titanium thin films with different thicknesses. These results were obtained by using the waveguide technique, according to schedule in Fig. 2b, which shows that the slender film (25 nm) presents attenuation values near 45% in the frequency range analysed and thicker films (>100 nm) behave as less efficient microwave absorbers.

The curve observed in Fig. 4 can be represented by a polynomial function, as shown in Eq. 2, where *a* and *b* are constants, equals to 240.9 and -0.62, respectively. Based on such equation, it is possible to estimate that titanium films with thickness values near 4.0 nm attenuate nearby 100% of the incident electromagnetic wave. This behavior is explained by the increase of defects in the

crystalline structure of the nanofilm as the thickness decreases, which favors the losses in the metallic film, as cited in the literature (Bosman, Lau and Gilgenbach, 2003; 2004; Shubin *et al.*, 2000).

$$y = a \cdot x^b \tag{2}$$

where:

y: represents attenuation (%);
x: represents thickness (nm) and
a and *b*: are constants (240.9 and -0.62, respectively).

From the electric resistivity measurements of the titanium thin films by using the four-point resistivity technique and the thickness of the films, the skin depth parameters were calculated according to Eq. 1 for 8 and 12 GHz. The skin depth calculated, the electric resistivity (*ρ*), and the superficial resistance (*R*) are presented in Table 2.

Table 2 shows that the electric resistivity decreases as the thickness increases. When correlating these results with the curve in Fig. 3, it is verified that larger attenuation of electromagnetic wave energy is associated with the thinner films. This behavior is explained by the thickness increase to be related to the lower electric resistivity, which diminishes the losses and consequently the attenuation. Thus, films with smaller thickness provide more effective microwave absorbers, in agreement with Machlin (1998). This behavior is better observed in Table 3, which presents the thickness in function of the average absorption. Table 2 also shows that the thickness of the films is much smaller than the calculated skin depth.

Table 2. Skin depth values of titanium thin films with different thicknesses.

Time of deposition (s)	Thickness x 10 ⁹ (m)	Surface resistance (Ω)	ρ x 10 ⁶ (Ω.m)	δ x 10 ⁵ (m) (f=8 GHz)	δ x 10 ⁵ (m) (f=12 GHz)
5±1	25±5	117	132	6.47	5.28
10±1	50±5	28.0	6.34	1.41	1.15
15±1	75±5	19.7	6.69	1.45	1.18
20±1	100±5	6.51	2.53	0.89	0.73

Table 3. Microwave absorption and thickness of titanium thin films.

Thickness (nm)	Average absorption (%)
25±5	44.3
50±5	33.0
75±5	40.1
100±5	17.8

Table 4. Electronic mobility of titanium thin films with different thicknesses.

Thickness (nm)	Electronic mobility (μ _e) (cm ² /V-s)
25±5	0.708
50±5	1.11
75±5	6.94
100±5	17.3

The electric behavior of the titanium thin films was also evaluated by Hall effect technique. Table 4 shows the electronic mobility of the studied films and it is observed that this property increases as the thickness increases, meaning that the electron mobility is favored in thicker films. This behavior suggests that thicker films begin to show the characteristics of the bulk metal, i.e., a reflector material. For thinner films, the electron mobility is diminished favoring the losses as heat by Joule effect, as mentioned by Nohara (2003).

These results show that titanium thin films behave more efficiently as microwave absorbers when there is thickness around 25 nm. This behavior is associated with the Eddy current formation on the film surface and it is also the lowest electronic mobility that favors the losses.

Figure 5 shows the reflectivity measurements of the titanium thin films with different thicknesses, obtained in different deposition times. The curves showed in Fig. 5a were obtained by using the setup depicted in Fig. 2a, while Fig. 4b presents the curves obtained in the setup showed in Fig. 2b. Figure 5a shows the behavior of thin film with 25 nm, where absorption values between 40 to 50% in all frequency range (8-12 GHz) are observed. Samples with larger thicknesses present lower absorption values, but nearly constant in all frequency range evaluated. Curves of samples prepared with thicknesses larger than 150 nm are not presented because they show similar behaviors, with absorption values between 5 and 10%.

Figure 5b presents the reflectivity measurements using an aluminum plate (100% reflector) under the thin films

(setup in Fig. 2b). These curves show the maximum absorption value and the frequency where this event occurs. These data confirm the dependence of microwave attenuation with the thin film thickness, and they also present a slight variation of the maximum attenuation with the frequency (8.6-9.0 GHz), according to the thin film thickness.

CONCLUSION

The TMS proved itself as a suitable technique to obtain titanium thin films, which perform efficiently as RAM. Reflectivity results from the waveguide technique (8-12 GHz) of the processed metallic thin films, with thickness range from 25 to 100 nm, show microwave attenuation values around 50% in broadband (8-12 GHz). These attenuation results are attributed to the electric resistivity and electronic mobility of the titanium thin films. The reflectivity results show that the maximum attenuation value (around 50%) occurs for thinner films (25 nm), which also present lower resistivity and electronic mobility that favor the losses.

ACKNOWLEDGMENTS

The authors acknowledge the financial support of *Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP)*, process no. 05-01258-05; *Financiadora de Estudos e Projetos (FINEP)*, process no. 1757-03; and National Council of Technological and Scientific Development (CNPq), processes no. 305478/2009-5 and 311396/2006-2; and also UDESC for providing the TMS equipment; *Laboratório de Materiais e Feixes Iônicos (LAMFI)* for the RBS analyses; *Laboratório de Sistemas Integráveis (LSI)*

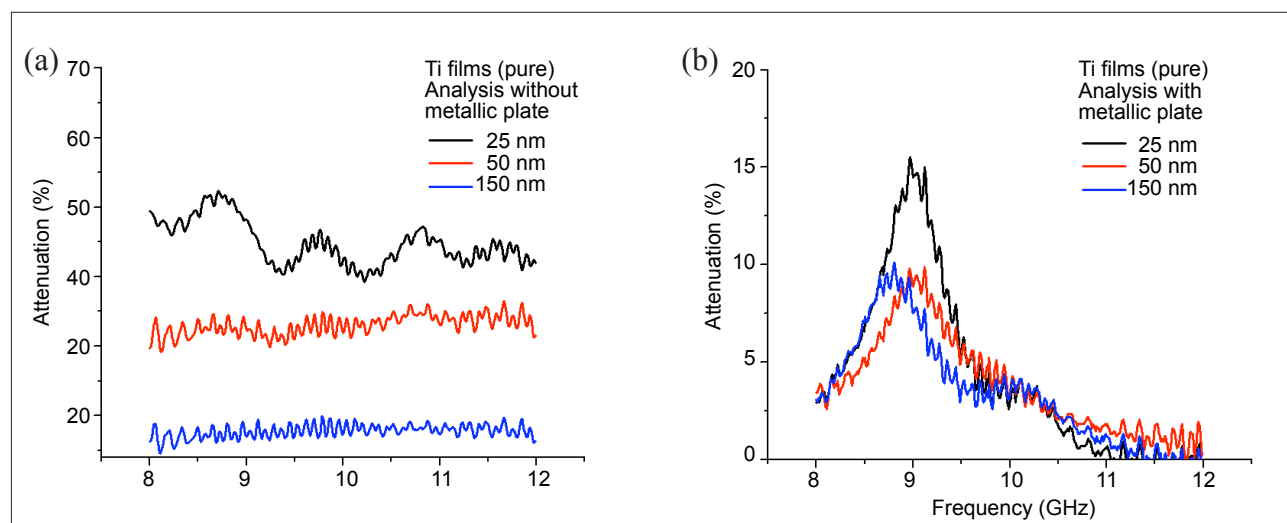


Figure 5. Attenuation curves of titanium thin films deposited at different times: (a) without metal plate (intrinsic absorption); (b) with metal plate (reflectivity measurements).

from USP/SP for the electric resistivity and perfilometry analyses; and *Laboratório de Semicondutores (LabSem)* of PUC/RJ for the Hall effect analyses.

REFERENCES

Balanis, C.A., 1989, "Antenna Theory: analysis and design". John Wiley Sons, New York, USA.

Bhat, K.S., Datta, S.K. and Suresh, C., 1998, "Electrical and microwave characterization of kanthal thin films: temperature and size effect", *Thin Solid Films*, Vol. 332, No. 1-2, pp. 220-224. doi:10.1016/S0040-6090(98)01103-1.

Biscaro, R.S., Rezende, M.C. and Faez, R., 2008, "Influence of doped polyaniline on the interaction of Pu/PAni blends and on its microwave absorption properties", *Polymers for Advanced Technologies*, Vol. 19, No. 2, pp.151-158. doi: 10.1002/pat.990.

Bosman, H., Lau, Y.Y., Gilgenbach, R.M., 2003, "Microwave Absorption in a Thin Film", *Applied Physics Letters*, Vol. 82, No. 9, p.1353. doi:10.1063/1.1556969.

Bosman, H., Lau, Y.Y., Gilgenbach, R.M., 2004, "Power absorption by thin films on microwave windows", *IEEE Transactions on Plasma Science*, Vol. 32, No. 3, pp. 1292-1297. doi:10.1109/TPS.2004.827579.

Bregar, V.B., 2004, "Advantages of Ferromagnetic Nanoparticle Composites in Microwave Absorbers", *IEEE Transactions on Magnetics*, Vol. 40, No. 3, pp. 1679-1684. doi: 10.1109/TMAG.2004.826622.

Bubert, H., Jenett, H., 2002, "Surface and Thin film Analysis", *Institute of Spectrochemistry and Applied Spectroscopy (ISAS)*, Wiley-VCH, Germany, 336p.

Doolittle, L.R., 1985, "Nuclear Instrument Method – Rump simulation code", B9, pp. 344-351.

Folgueras, L.C., Rezende, M.C., 2007, "Hybrid multilayer structures for use as microwave absorbing material" *Proceedings of the SBMO/IEEE MTT-S International Microwave & Optoelectronics Conference*, Brazil, pp. 483-487.

Fontana, L.C., Muzart, J.L.R., 1998, "Characteristics of triode magnetron sputtering: the morphology of deposited titanium films", *Surface and Coatings Technology*, Vol. 107, No. 1, pp. 24-30. doi:10.1016/S0257-8972(98)00576-3.

Fortunato, E., Nunes, P., Costa, P.D., Brida, D., Ferreira, I. and Martins, R., 2002, "Characterization of aluminium doped zinc oxide thin films deposited on polymeric substrates", *Vacuum*, Vol. 64, pp. 233-236. doi:10.1016/S0042-207X(01)00319-0.

Hashish, E.A., 2002, "Design of wideband thin layer planar absorber", *Journal of Electromagnetic Waves and Applications*, Vol. 16, No. 2, pp. 227-241. doi: 10.1109/APS.2011.5997137.

Ishii, N., Yasaka, Y., 2004, U.S.Patent N° 6823816. Available at: www.patents.com/us-6823816.html.

Kaiser, K.L., 2004, "Electromagnetic Compatibility Handbook", CRC Press, Boca Raton, USA.

Machlin, E.S., 1998, "Materials Science in Microelectronics", Elsevier, 2a ed., New York, Vol. 2, pp. 1-70.

Mayes, E., 2006, U.S. Patent N° 6986942. Available at: www.patents.com/us-6986942.html.

Mikhailovsky, L.K., 1999, "Solution of actual problems of electromagnetic compatibility by means of Spin (Non-Current) Electronics and Non-phase Electrodynamics", *Proceedings of the VIII International Conference on Spin Electronics – Section of International Conference on Gyromagnetic Electronics and Electrodynamics*, Vol. 13-16, Moscow Region, Fisanovka, Rússia, pp. 327-349.

Nicolson, A. M., Ross, G. F., 1970, "Measurement of the Intrinsic Properties of Materials by Time Domain Techniques", *Instrumentation and Measurement*, Vol. 19, pp.377-382. doi: 10.1109/TIM.1970.4313932 .

Nie, Y., *et al.*, 2007, "The electromagnetic characteristics and design of mechanically alloyed Fe-Co particles for electromagnetic-wave absorber", *Journal of Magnetism and magnetic materials*, Vol. 310, pp.13-16. doi:10.1016/j.jmmm.2006.07.021

Nohara, E.L., 2003, "Materiais Absorvedores de Radiação Eletromagnética (8-12 GHz) Obtidos pela Combinação de Compósitos Avançados Dielétricos e Revestimentos Magnéticos". Ph.D. Thesis, Technological Institute of Aeronautics, São José dos Campos, S.P., Brazil.

Ohring, M., 1991, "The Materials Science of Thin Films", Stevens Institute of Technology, Department of Materials Science and Engineering, Hoboken, New Jersey, Academic Press, San Diego, pp. 531.

Rezende, M.C., Silva, F.S. and Martin, I.M., 2000, "Materiais absorvedores de radiação eletromagnética", *Spectrum*, Vol. 2, pp. 17-20.

Salmon, L.G., 1993, "Evaluation of thin film MCM materials for high-speed applications", *IEEE Transactions on Components, Hybrids, and Manufacturing Technology*, Vol. 16, No. 4, pp. 388-391. doi: 10.1109/33.237934.

Serway, R.A., 1998, "Principles of Physics", Saunders College Texas, Fort Worth, London.

Shubin, V.A., *et al.*, 2000, "Local electric and magnetic fields in semicontinuous metal films: beyond the quasistatic approximation", *Physical Review B*, Vol. 62, No. 16, pp. 11230-11244. doi: 10.1103/PhysRevB.62.11230.