Optical Characterization of Ultra-Thin Iron and Iron Oxide Films

David Nečas,† Lenka Zajičková, Daniel Franta, and Pavel Štaheľ
Department of Physical Electronics, Faculty of Science,
Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

Petr Mikulík and Mojmir Meduňa
Department of Condensed Matter Physics, Faculty of Science,
Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

Miroslav Valtr
Czech Metrology Institute, Okružní 31, 638 00, Brno, Czech Republic

(Received 3 June 2008; Accepted 13 November 2008; Published 4 April 2009)

Ultra-thin films of ⁵⁷Fe deposited on silicon substrates and SiO₂·C₆H₅ support layers and subsequently oxidized in laboratory atmosphere are studied by two optical methods: the combination of UV/VIS/NIR spectroscopic ellipsometry and spectrophotometry, used to find layer thicknesses and optical constants, and X-ray specular reflectometry, used to obtain the electron density depth profile. The results of both methods are compared and found to be in a relatively good agreement. [DOI: 10.1380/ejssnt.2009.486]

Keywords: Iron; Iron oxide; Thin films; Ellipsometry; Spectrophotometry; X-ray reflection

I. INTRODUCTION

Ultra-thin films of transition metals restructured into nanoparticles can be used in surface-bound chemical vapor deposition of carbon nanotubes (CNTs) [1, 2] because the CNTs start to grow from the nanoparticles [3, 4]. Metal surfaces and their oxidation have been extensively investigated in situ at UHV/HV conditions [5] and in pure oxygen atmosphere [6], respectively. However, the application of metal films as catalysts for the synthesis of CNTs reveals the needs to study them after exposure to air and subsequent activation for the CNT growth. The key factor is the thickness of the ultra-thin metal film because it influences the size of nanoparticles after activation that is correlated with the nanotube diameter [1, 2].

Although the thickness of metal film can be monitored in situ by a quartz-crystal-balance thickness monitor it is necessary to verify the results in case of ultra-thin films. The commonly used method is to pattern the metal film and measure the height of the created step by atomic force microscopy (AFM). However, this method requires additional processing steps and it cannot be used on the same sample actually used for the CNT deposition. Moreover, the required sub-nanometer precision is difficult to achieve due to the step and surface imperfections. Therefore, it is useful to test other non-destructive methods based on the optics of thin films. The combination of UV/VIS/NIR spectroscopic ellipsometry and spectrophotometry is a powerful thin film characterization technique, however, in the case of ultra-thin films its sensitivity may be limited. In this paper, it is, therefore, applied in combination with X-ray specular reflectance and the results are compared.

II. EXPERIMENTAL

Two studied samples, denoted 57Fe1 and 57Fe2, consisted of iron film deposited either on polished c-Si substrate or SiO₂·C₆H₅ support layer on c-Si. The c-Si was a 345 μm thick silicon wafer of semiconductor purity (2–4 Ω cm, (100)). The ultra-thin iron films were prepared by vacuum evaporation of iron enriched to 90% by ⁵⁷Fe isotope. The Fe was evaporated from the W boat at the operation pressure not exceeding 1.1×10⁻³ Pa. The thickness of the films was monitored in situ by quartz balance crystal in the frequency range 5.1–6.1 MHz. This thickness, equal to 10 nm, will be referred further on as the nominal thickness. Both films were exposed to laboratory atmosphere for one year.

The support SiO₂·C₆H₅ film was deposited by plasma enhanced chemical vapour deposition (PECVD) in radio frequency (RF) capacitive discharge from 8% hexamethyldisiloxane in oxygen. The pressure, RF power and DC self-bias were 22 Pa, 100 W and –90 V, respectively. The film was calcinated in vacuum at 970 K for 30 min. More details can be found in [7, 8].

The optical measurements were performed using a spectroscopic phase modulated Jobin Yvon UVISEL ellipsometer and spectrophotometer PerkinElmer Lambda 45. The ellipsometric measurements were carried out for five angles of incidence in the interval 55–75° within the spectral region of 190–2100 nm (0.6–6.5 eV). The reflectance measurements were performed for the angle of incidence of 6° in the spectral region of 190–1000 nm (1.24–6.5 eV).

X-ray specular reflectance was measured by means of a high-resolution X-ray diffractometer using CuKα₁ radiation. The beam was monochromatized and collimated by a laterally graded parabolic multilayer mirror in order to obtain high intensity flux. A Bartels monochromator (Ge 220 crystals) was used for additional elimination of CuKα₂ and CuKβ lines, so the divergency of the beam was 0.003°. The primary beam was further limited by slits of 0.4×6 mm size. The intensity counts were recorded by a scintillation detector with a 0.4 mm slit in order to select only the specularly reflected signal.
The associated ellipsometric parameters \( I_\theta \), \( I_\phi \) and reflectance \( R \) of samples 57Fe1 and 57Fe2 obtained in UV/VIS/NIR region were calculated using the matrix formalism [10] and fitted simultaneously using the multisample modification of the Marquart-Levenberg least squares method (LSM).

The input data of the multisample method actually consisted of three data sets, i.e. measurements on

(i) sample 57Fe1 – \( ^{57} \text{Fe} \) on c-Si,
(ii) sample 57Fe2 – \( ^{57} \text{Fe} \) on \( \text{SiO}_x \text{C}_y \text{H}_z \), and
(iii) \( \text{SiO}_x \text{C}_y \text{H}_z \) – the support \( \text{SiO}_x \text{C}_y \text{H}_z \) layer of 57Fe2 on c-Si.

The structural model of 57Fe1 consisted of three layers:

(i) top iron oxide layer,
(ii) \( \text{Fe} \) layer, and
(iii) native oxide layer (NOL) on c-Si.

The structural model of 57Fe2 contained the \( \text{SiO}_x \text{C}_y \text{H}_z \) layer in place of the NOL. Although the NOL was not removed prior to \( \text{SiO}_x \text{C}_y \text{H}_z \) deposition, it was not considered separately because of similar optical constants. The schematic diagrams of the structural models used for 57Fe1, 57Fe2 and \( \text{SiO}_x \text{C}_y \text{H}_z \) are in Fig. 1.

The experimental optical data on the ultra-thin films do not contain enough information to fit the detailed structure of the dielectric function of the individual layers. Therefore, the optical constants of the layers were described using relatively simple dispersion models in order to keep the total number of fitted parameters low and the fitting stable:

(i) The optical constants of the iron oxide overlayer were modelled by a one-term parameterized joint density of states (PDOS) model [11].
(ii) The optical constants of the Fe layer were modelled by sums of Lorentz oscillators, i.e. by the sum of the Drude term (corresponding to the dielectric response of free carriers) and one additional Lorentzian term.
(iii) The dielectric response of the \( \text{SiO}_x \text{C}_y \text{H}_z \) and NOL were described by the parameterized density of states (PDOS) model according to [11].

The spectral dependences of the c-Si substrate optical constants were taken from the literature [12] and fixed within the LSM.

Within the multisample method used for simultaneous fitting of all three data sets, both thickness and optical constants of the corresponding layers in each set were assumed to be identical with the exception of the support layer thickness which was permitted to differ between 57Fe2 and \( \text{SiO}_x \text{C}_y \text{H}_z \).

B. X-ray specular reflectance

X-ray specular reflectance is sensitive to electron density of the material, thickness of the layer and the interface roughness. The electron density \( \rho \) determines the complex index of refraction \( \hat{n} \) usually expressed in the form [13]

\[
1 - \hat{n} = \delta + i \beta \propto \rho(z) .
\]

The imaginary part of \( \hat{n} \) can be often neglected for very thin layers and an electron density profile \( \rho(z) \) of a layered structure can be determined assuming only one material of substrate with varying electron density in \( z \) direction perpendicular to the surface. In that case a relative electron density of the layer is defined as a ratio with respect to the relative electron density of the substrate.

The specular reflectance curves were simulated using a matrix optical formalism [14] for a finite system of \( N \) layers with thicknesses \( d_j \). The planar interfaces were substituted by rough interfaces with a rms roughness \( \sigma_j \) on the layer top, i.e. the Fresnel coefficients for ideal interfaces \( r_j \) were modified by the Debye-Waller factor [15].

The experimental data obtained on sample 57Fe2 were independently fitted by two models:

(i) A 3-layer model with independent layer thicknesses, roughnesses and electron densities relative to Si, i.e. 10 parameters in total. This model is easier to fit, however, it might not be suitable if the profile of layer in \( z \) direction is not rectangular or the interface roughness is not Gaussian.
(ii) A model of 30 layers with a fixed thickness 1 nm and identical interface roughnesses of all layers. In other words, only the individual electron densities and the common roughness were fitted.

The mass density difference of Si and \( \text{SiO}_2 \) is at about 5%, thus the interference from the interface between \( \text{SiO}_x \text{C}_y \text{H}_z \) and Si plays a negligible role compared to the scattering from the dense iron layer.

IV. RESULTS AND DISCUSSION

The ellipsometric and reflectance data of all three samples are shown in Fig. 2. It can be seen that the agreement between the model and experimental data is sound.

The spectral dependences of optical constants of the support \( \text{SiO}_x \text{C}_y \text{H}_z \) layer are shown in Fig. 3. This material is not \( \text{SiO}_2 \) because it exhibits weak absorption in measured range and slightly higher refractive index. These optical constants are typical for organosilicon plasma polymers containing hight amount of \( \text{SiO}_x \) [16].
The thicknesses of the layer were 333 and 335 nm for samples SiO\textsubscript{x}C\textsubscript{y}H\textsubscript{z} and 57Fe\textsubscript{2}, respectively.

The NOL was at first fitted independently, however, its thickness and optical constants were strongly correlated and the fit resulted in non-physical values. Therefore, the NOL material was assumed to have the optical constants as SiO\textsubscript{x}C\textsubscript{y}H\textsubscript{z}. Then, the NOL thickness was 3.5 nm, i.e. it represented an effective layer consisting of the actual NOL and a transitional layer to the Fe film.

After exposure of iron thin films to atmosphere a native oxide layer is formed on the top. According to [17] the typical thickness of this layer is 1–2 nm and it is formed by Fe\textsubscript{2}O\textsubscript{3}. However, our measurement by conversion electron Mossbauer spectroscopy [18] performed on sample 57Fe\textsubscript{2} detected only Fe\textsuperscript{3+} whereas Fe\textsuperscript{0} was below the detection limit. Therefore, it is not clear how thick is the oxide layer in case of our samples and two-layer model of iron was applied for the processing of the UV/VIS/NIR optical data. These two layer must be understood as effective layers representing iron oxidized to various degree.

The thicknesses of the top and bottom layers were 4.8 and 15.6 nm, respectively, i.e. the total film thickness was 20.4 nm. The spectral dependences of their optical constants are shown in Figs. 4 and 5. The bottom layer exhibits a typical metallic behaviour, manifested by the dominant Drude term. Nevertheless, comparing the obtained optical constants with tabulated data in Palik [19], it can be concluded that the bottom film is not pure Fe. The top layer, according to its optical constants, has oxide character, i.e. refractive index in the range 1.3–1.7.
FIG. 6: Angular dependence of X-ray reflectance of sample 57Fe2. Label exp denotes the experimental data; 3-layer denotes the simple 3-layer model while profile denotes modelling of the electron density profile using 30 independent layers.

FIG. 7: Relative electron density profile of sample 57Fe2, determined using the 30-layer model. Symbol d denotes depth, electron density $\rho$ is relative to c-Si.

with normal dispersion up to 5.4 eV and relatively low extinction coefficient. Since the absorption peaks of the different iron oxide phases in the UV/VIS region almost overlap with each other [20], the simple dispersion model did not permit to determine the particular phase. The top layer partially represents also a fine roughness of the film (residue of an island character observed for smaller thicknesses [21]), which contributes to its low effective refractive index.

The measured specularly reflected X-ray intensity for sample 57Fe2 is shown in Fig. 6. Analyzing the period of oscillation in the reflectance curve and assuming only one layer on top of SiO$_x$C$_y$H$_z$ without specifying the layer material yields the total layer thickness of 15.2 nm. The red curve in Fig. 6 shows the fit with the 3-layer model. It yielded the total film thickness of 18.2 nm, however the fit is inadequate.

The green curve in Fig. 6 shows the simulation after the fit using the 30-layer model. The resulting electron density profile $\rho(z)$ is shown in Fig. 7. It is evident that a layer of Fe with total thickness around 15 nm is present. However, the obtained result shows that the Fe layer is not homogeneous in the $z$ direction. The partially decreased electron density in the area of 5 nm from the top surface can correspond to an iron oxide layer. A significantly decreased $\rho(z)$ for depths from 15 nm to 22 nm can correspond to a transitional layer between SiO$_x$C$_y$H$_z$ and Fe. The short period oscillations in $\rho(z)$ correspond to the closest step in layer thickness of 1 nm which is already almost at the resolution limit. Therefore the instability of the electron density profile in depths greater than 24 nm, i.e. the substrate, is an artifact of the method and can be disregarded.

Comparing the results of UV/VIS/NIR optical methods and X-ray reflectometry, it can be concluded that these two methods are not sensitive to the same film properties and both require substantial modelling. Despite of this fact they are quite consistent as concerns the total iron film thickness. It increases the reliability of the results. Both the methods showed that the nominal thickness was, in this case, underestimated. One possible reason could be a film thickness increase due to its oxidation [21]. However, it can hardly explain twofold increase of the film thickness that can be attributed also to problems in quartz balance crystal measurement.

V. CONCLUSION

Ultra-thin films of $^{57}$Fe deposited on silicon substrates and SiO$_x$C$_y$H$_z$ support layers and subsequently oxidized in laboratory atmosphere were studied using two optical methods: (i) the combination of UV/VIS/NIR spectroscopic ellipsometry and spectrophotometry, (ii) X-ray specular reflectometry. If the oxidation state of the oxidized iron films is not known ellipsometry is not able to determine their inner structure because of strong correlation between optical constants and thickness for ultra-thin films. Nevertheless, it can determine the total film thickness relatively well under the approximation of effective layers. If a set of samples with different thicknesses and the same structure was available the situation could be improved by using the multi-sample method. The X-ray reflectance is obviously able to determine the thickness because it is not so sensitive to material changes. However, the model of 30 layers showed that for correct fitting of the data the actual structure of the film has to be taken into account, although in this case it is not clear how to define the iron/iron oxide film from the electron density profile. Anyway, the layer thickness determined by both methods was found to be greater than that given by the quartz crystal balance in-situ monitor.

Acknowledgments

This work was supported by the Ministry of Education, Youths and Sports of Czech Republic under contracts MSM 0021622411 and MSM 0021622410 and by Academy of Sciences of Czech Republic under contract KAN311610701.

[1] M. Chhowalla, K. B. K. Teo, C. Ducati, N. L. Rupesinghe, G. A. J. Amarasinghe, W. I. Milne, J. Appl. Phys. 90, 5308–5317 (2001).
[2] Y. Y. Wei, G. Eres, V. I. Merkulov, D. H. Lowndes, Appl. Phys. Lett. 78, 1394–1396 (2001).
[3] M. Meyyappan, L. Delzeit, A. Cassell, D. Hash, Plasma Sources Sci. Technol. 12, 205–216 (2003).
[4] Y. M. Li, W. Kim, Y. G. Zhang, M. Rolandi, D. W. Wang, H. J. Dai, J. Phys. Chem. B 105, 11424–11431 (2001).
[5] H. Lüth, Solid Surfaces, Interfaces and Thin Films, Springer, Berlin, 2001.
[6] N. Birks, G. H. Meier, F. S. Pettit, Introduction to the High Temperature Oxidation of Metals, Cambridge University Press, Cambridge, 2006.
[7] L. Zajíčková, V. Buršíková, D. Franta, A. Bousquet, A. Granier, A. Goullet, J. Buršík, Plasma Processes and Polymers 4, S287–S293 (2007).
[8] L. Zajíčková, V. Buršíková, Z. Kučerová, J. Francelová, P. Stáhel, V. Peřina, A. Macková, J. Phys. Chem. Solids 68, 1255–1259 (2007).
[9] O. Acher, E. Bigan, B. Drévilleon, Rev. Sci. Instrum. 60, 65–67 (1989).
[10] I. Ohldal, D. Franta, Ellipsometry of thin film systems, in: E. Wolf (Ed.), Progress in Optics, Vol. 41, Elsevier, Amsterdam, 2000, pp. 181–282.
[11] D. Franta, D. Nečas, L. Zajíčková, Opt. Express 15, 16230–16244 (2007).
[12] C. M. Herzinger, B. Johns, W. A. McGahan, J. A. Woollam, W. Paulson, J. Appl. Phys. 83, 3323–3336 (1998).
[13] B. L. Henke, E. M. Gullikson, J. C. Davis, Atomic Data And Nuclear Data Tables 54, 181–342 (1993).
[14] M. Born, E. Wolf, Principles of Optics, Pergamon Press, London, 1965.
[15] P. Croce, L. Nevot, Reuvle de Physique Appliquee 11, 113–125 (1976).
[16] L. Zajíčková, V. Buršíková, Z. Kučerová, D. Franta, P. Dvořák, R. Šmíd, V. Peřina, A. Macková, Plasma Sources Sci. Technol. 16, S123–S132 (2007).
[17] T. Shinjo, T. Iwasaki, T. Shigematsu, T. Takada, Jpn. J. Appl. Phys. 23, 283–285 (1984).
[18] O. Jašek, O. Schneeweiss, B. David, L. Zajíčková, M. Vondráček, Study of nanocrystalline iron phases on Si-SiO$_2$/Fe MWCNT samples, in: Proceedings of NANO ’07, Brno, Czech Republic, 2007, p. 65.
[19] D. W. Lynch, W. R. Hunter, Metals, in: E. D. Palik (Ed.), Handbook of Optical Constants of Solids II, Academic Press, Inc., 1985, pp. 385–396.
[20] R. M. Cornell, U. Schwertmann, The Iron Oxides: Structure, Properties, Reactions, Occurences and Uses, Wiley, Weinheim, 2003.
[21] S. Hofmann, M. Cantoro, B. Kleinsorge, C. Casiraghi, A. Parvez, J. Robertson, C. Ducati, J. Appl. Phys. 98, 034308 (2005).