Preparation and Characterization of Electrodeposited Co/p-Si Schottky Diodes

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ABSTRACT

Schottky diodes were prepared by photoinduced electrodeposition of Co on p-Si, probing the influence of different concentrations of $CoSO_4$ (26 and 104 mM) in the electrolyte on the electrical properties of the metal-semiconductor interface. Current density versus voltage (JxV) and capacitance versus voltage (CxV) measurements were performed in diodes with different Co thicknesses to obtain the barrier heights and ideality factors. Atomic force microscopy (AFM) and vibrating sample magnetometry (VSM) were additional techniques used to determine the surface morphology and the magnetic response. Devices with improved electrical properties were observed by increasing the thickness of the metal, i. e., saturation currents with values of about 0.1 $mA.cm^{-2}$, ideality factors close to 1.19 and barrier heights of about 0.65 eV were determined.

Index Terms: Electrodeposition, Schottky junction, metal-base transistor, spintronic devices.

1. INTRODUCTION

Metal-semiconductor (MS) structures exhibiting a potential barrier at the interface are the base for the study of different kinds of devices and are known as Schottky diodes (due to the current rectifying behavior). MS interfaces fabricated with magnetic metallic layers, with or without rectifying effect, attract special interest for the development of spintronic devices [1-3]. The fabrication of a magnetic metal base transistor (MBT), a device with Schottky barriers at emitter/base and base/collector interfaces, similar to the spin transistor proposed by Monsma et. al. [4], was the subject of previous works [2, 3]. The base and the emitter of the TBMs were electrodeposited sequentially on the surface of a p-type Si single crystal substrate (collector). The electrodeposition of the magnetic base, Co in this case, is an important issue for the device performance and will be explored in this work from the point of view of the electrochemical deposition process and morphological, magnetic and electrical characterization.

Electrodeposited Schottky diodes on Si have presented improved rectifying properties when compared to evaporated metal layers, as observed in the Ni/Si system by Kiziroglou et. al. [5]. The electrodeposition of metals on p-type Si is a process that requires photoinduced electrons, i.e., the electrochemical reactions only occur in the presence of light sources [6, 7]. The electrochemical deposition of Co on p-Si has been recently extensively studied by Muñoz [8].

2. EXPERIMENTAL PROCEDURE

The substrate used as working electrode during the electrodeposition was p-type silicon (B doped) with (100) orientation, 5 – 25 Ω.cm resistivity and 600 – 650 μm thick. The silicon wafers were cleaned with de-ionized water to remove macroscopic particles from the surface. The native oxide on the surface of the substrates was removed by immersion in a 5% HF solution for 20 s and finally the sample was rinsed with de-ionized water for 10 s. After cleaning procedure, In-Ga eutectic alloy was applied on the back side of the Si substrate to obtain ohmic contact with the potentiostat terminals. The effective area for the Co deposition was 0.5 cm^2, defined with adhesive tape masks.

The electrolytes used were two aqueous solutions containing 26 mM $CoSO_4$ + 0.5 M Na_2SO_4 + 0.5 M H_3BO_3 and 104 mM $CoSO_4$ + 0.5 M Na_2SO_4 + 0.5 M H_3BO_3, both with an acid pH of 4.3. The electrochemical experiments were performed in a potentiostat Autolab PGSTAT30 using a saturated calomel electrode (SCE) as reference electrode and a Pt foil as counter electrode. The photoinduction process during electrodeposition was carried out with a conventional 100 W tungsten lamp, placed at a distance of 3.0 cm from the surface of the working electrode, corresponding to an illumination intensity of about 8900 W/m^2. The lamp provides an emission spectrum that could be considered as constant for wavelengths in the visible range.

For the electrical characterization, after deposition of cobalt on silicon an electrical terminal (copper wire) was fixed with conductive silver paste on the surface of the deposit. The second terminal for the electrical measurements was the contact at the back side of the sample, prepared previously for the electrodeposition step. The characteristic curves, current density versus voltage (JxV) and capacitance versus voltage (CxV), were obtained using the potentiostat, that permits to perform the voltage scanning, current acquisition and capacitance measurements. The last one is acquired by the potentiostat by superposing a small alternate signal (amplitude of 10 mV) to the voltage ramp. Additional morphological characterization and roughness measurements were performed with atomic force microscope (AFM). Magnetization curves were obtained using a vibrating sample magnetometer (VSM).

3. RESULTS

Voltammetries of the cobalt sulfate electrolyte with and without illumination are shown in Figure 1a. The electrolyte contains 104 mM of $CoSO_4$ and the voltages are negative, as expected for reduction of the Co^{2+} species. For the experiment conducted in the dark, no evidence of electrochemical current is obtained. However, in the presence of light the typical curve for the $Co^{2+} + 2e^- \rightarrow Co$ electrochemical reaction is observed, starting at about -0.55 V vs SCE. The voltammetric curve also shows no evidence of H_2 evolution, as normally occurs for voltages less negative than -1.5 V vs SCE and characterized by a fast increase of cathodic current, as usually seen for n-Si substrates [9], indicating a predominance of the Co^{2+} reaction over this process.

The film growth was controlled by potential (potentiostatic deposition). Figure 1b shows a current transient for an applied voltage of -0.8 V vs SCE. The current transient is typical for nucleation and growth processes on Si surfaces, with an initial nucleation peak and current saturation for long deposition times. The absence of H_2 evolution mentioned above corresponds to a process with 100% of efficiency for the Co reduction, allowing the calculation of the thickness of the metallic layer h with equation (1), where the charge Q is obtained by integrating the current transients. Other quantities of equation (1) are: the molecular mass M, the number of electrons in the electrochemical reaction n (2 for Co^{2+}), the electronic charge q, the Avogadro number N_A, the mass density ρ and the surface area A of the deposit.

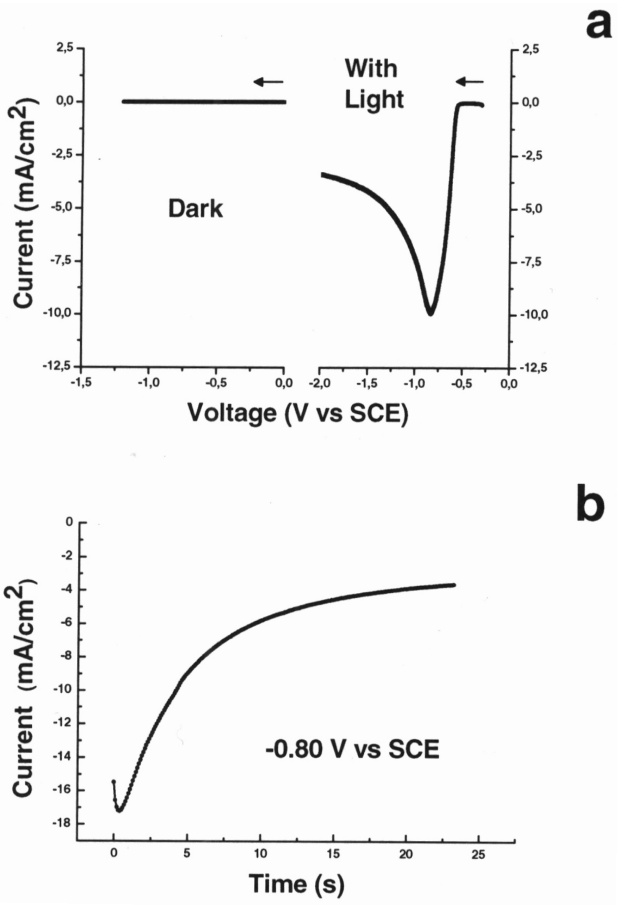

Figure 1. (a) Voltametries at 10 mV / s with and without illumination. (b) Current transient at -0.80 V vs SCE under illumination.

$$h = \frac{MQ}{nq\,N_A \rho A} \tag{1}$$

Figure 2 shows the results obtained with the VSM magnetic characterization of samples with different amounts of Co, where the thicknesses were varied by controlling the deposition time and calculated with equation (1). The Co deposits were prepared using a 104 mM Co sulfate bath. Figure 2a displays the hysteresis loop for a 110 nm thick Co sample with a coercive field of 50 Oe. The curve in Figure 2b shows the coercive field as a function of Co thickness, evidencing higher coercivity for lower thicknesses, reaching values in the range of 325 to 50 Oe, similarly to the observed in Co layers electrodeposited on n-Si [9].

The results from AFM measurements are exposed in Figure 3. The image in Figure 3a shows the morphology of the surface of a Co sample with thickness of 138 nm, with the formation of irregular grains. From similar images was possible to calculate the root mean square roughness of the surface as a

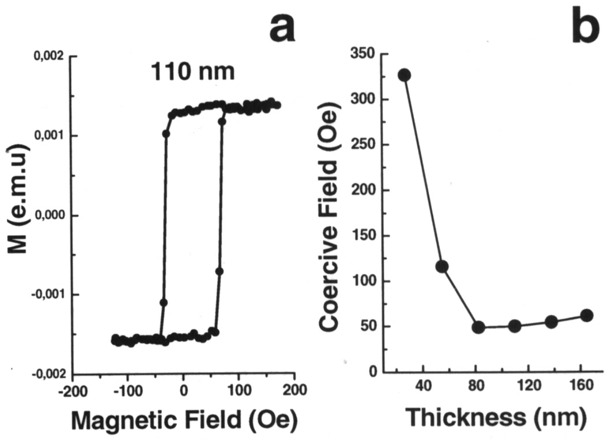

Figure 2. (a) Magnetization curve for a 110 nm thick Co film, with coercivity of 50 Oe. (b) Coercive field measured by magnetization curves as a function of film thickness.

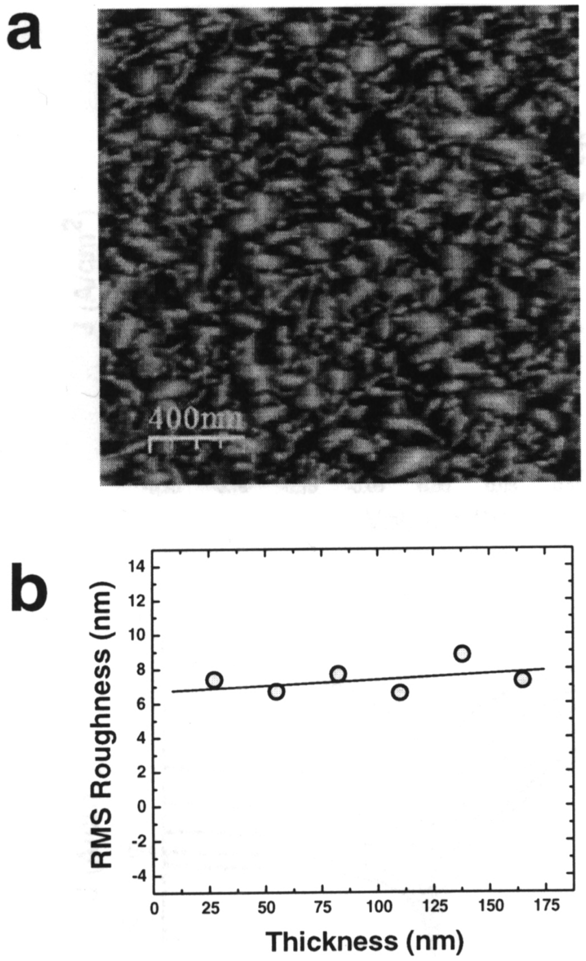

Figure 3. (a) AFM image of the surface of a 138 nm thick Co film. (b) Evolution of the measured root mean square roughness with film thickness

function of the thickness, as shown in Figure 3b. Roughnesses of about 8 nm were obtained for thicknesses varying in the range of 25 to 165 nm, indicating that the ratio between the roughness and the thickness of the samples decreases by increasing the deposition time.

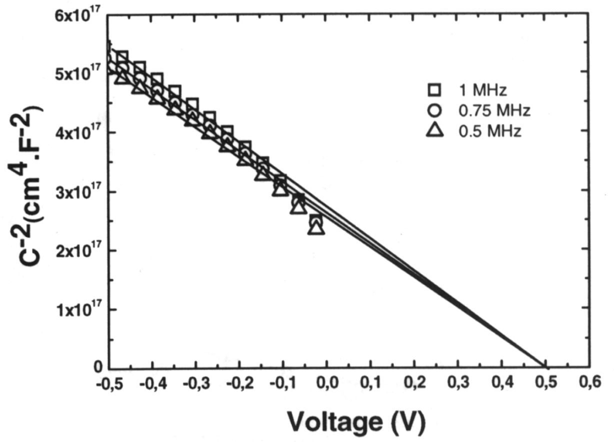

Figure 4. Capacitance versus voltage measurements of a 165 nm thick Co film on p-Si.

Figure 4 shows capacitance measurements for three different frequencies (0.50, 0.75 and 1.00 MHz) as a function of the applied voltage of a 165 nm thick Co layer on p-Si. The capacitance behavior is characteristic of diode interfaces with finite values for negative voltages applied to the semiconductor electrode. The plot of C^{-2} versus V decays linearly with the voltage intensity indicating the dependence of the depletion length with potential. The barrier height can be calculated through equation (2), as described in detail in reference 10, where V_1 is obtained by extrapolating the linear regime to zero values for the vertical axis, k is the Boltzmann constant, q the electronic charge, T the temperature in Kelvin and ξ is the potential difference between conduction band and Fermi level of p-Si substrate. The determined value of about 0.76 eV for Φ_b is roughly independent of the measuring frequency and its magnitude will be compared below with results from (JxV) curves.

$$\Phi_b = V_1 + \xi + \frac{kT}{q} \qquad (2)$$

Figure 5a shows the semilog JxV characteristics of six electrodeposited Co/p-Si diodes with increasing Co thickness from 28 to 165 nm, prepared with the solution containing lower concentration of cobalt sulfate (26 mM). In Figure 5c similar sequence of curves are shown, for the same sequence of Co thickness, from diodes electrodeposited with a higher concentration of $CoSO_4$ (104 mM) in solution. The figures show typical current – voltage behavior observed in p-type Schottky diodes, with a forward increase for positive voltages (positive in the semiconductor) and a constant reverse current for negative voltages (negative in the semiconductor). Both electrolytes exhibit a clear dependence between the Co thickness and the reverse current value, which reduces as the thickness grows. For thicknesses of 138 nm or higher, values of about 0.1 mA/cm² were obtained for this saturation current, a value lower than the existing in the literature for electrodeposited Co/p-Si Schottky junctions [3, 8].

In Figures 5b and 5d are shown the dependences of the magnitude of reverse and forward current densities as a function of the Co thickness, for samples prepared with both electrolytes, 26 and 104 mM. The figures show reverse and forward current densities in absolute values obtained at -1.0 V and 0.1 V, respectively. In these figures is evidenced that the dependence of current on thickness is not exclusive for the reverse polarization regime, occurring also when forward bias is applied. The dependence of the current with the thickness of the layers is a non expected result, and needs further investigation. It was reported previously in metal-semiconductor structures and explanations were based on quantum confinement [11] and on a dependence of the Richardson constant with the thickness of the metal layer [12]. However, in our case, for very thin layer of about 80 nm or less, the existence of uncovered areas of the substrate (pinholes) are expected due to the nucleation process during electrodeposition and in these regions the higher values of current could be attributed to edge effects. The presence of pinholes was confirmed in a previous work on electrodeposited MBT by AFM and electrical measurements [2]. Additionally, the formation of Schottky barriers by the silver paste in the pinholes cannot be neglected. However, the reverse current of these junctions is of about 2 orders of magnitude lower that the reverse current in Co/Si interfaces, as measured in this work (results not shown).

The thermionic emission theory [10] was applied to study the JxV characteristics, which describes the transport mechanism above the potential barrier in a Schottky junction and is resumed by the equation (3),

$$J = J_0 \exp(qV / nkT)[1-\exp(-qV / kT)] \qquad (3)$$

where V is the applied voltage and n is the ideality factor that accounts for deviations from this theory. J_0 is the saturation density current defined as,

$$J_0 = A^{**}T^2 \exp\{-q\phi_b/kT\} \qquad (4)$$

where f_b is the interface barrier height, and A^{**} is the Richardson constant equal to 32 $A.K^{-2}.cm^{-2}$ for p-type Si [13].

Figures 6 and 7 show the dependence of two important parameters of Schottky diodes with thickness of cobalt, barrier height and ideality factor, respectively. These parameters were obtained by adjusting JxV characteristics with equation (3). The results in Figure 6 show that the increase in thickness

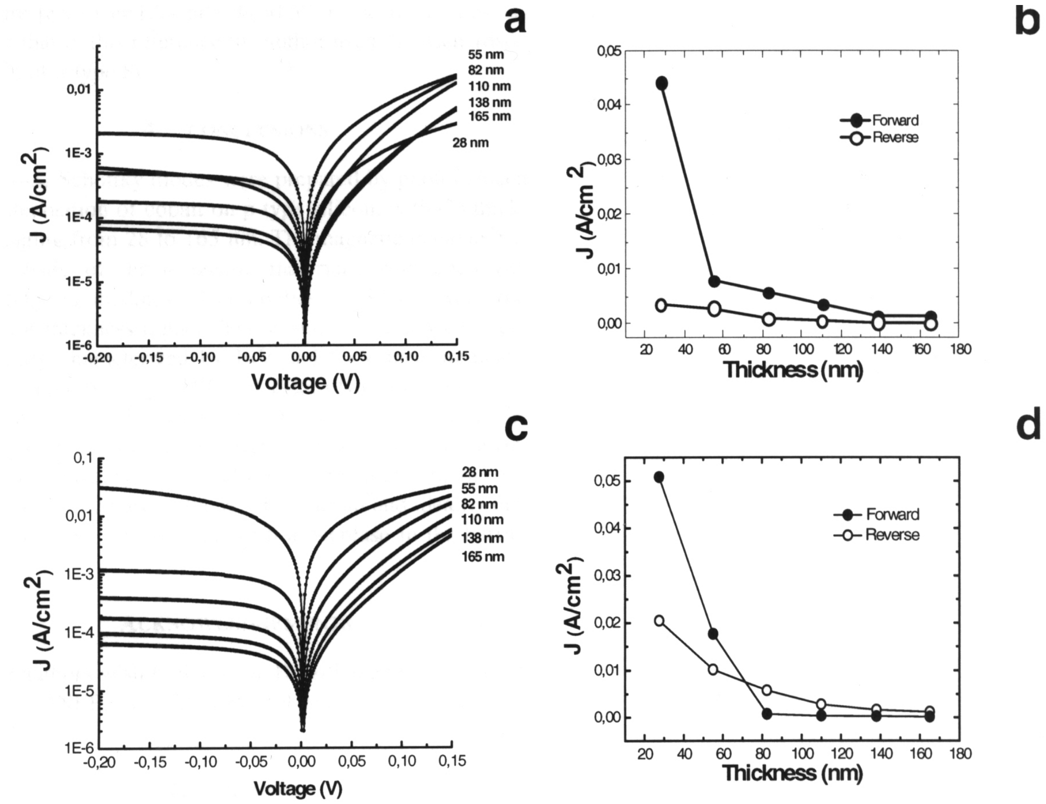

Figure 5. Current versus voltage curves for Co/p-Si diodes with various Co thickness, prepared from baths containing (a) 26mM and (c) 104mM of $CoSO_4$. Dependence of current values (forward and reverse) as a function of Co thickness, for both electrolyte concentrations of 26 (b), and 104 mM (d)

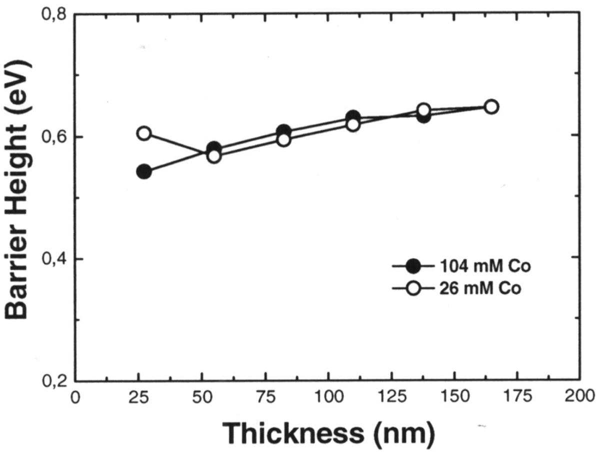

Figure 6. Barrier height calculated from thermionic emission theory approximation as a function of thickness of Co on Co / p-Si diodes, prepared with electrolytes containing two different amounts of $CoSO_4$

leads to an increase in the barrier height. In Figure 7 ideality factors tending to 1 were observed with the increase of cobalt thickness. The straight line at n=1 in this graphic represents the ideality factor of an ideal diode described by thermionic emission theory. From CxV experiments, shown in Figure 4, the barrier height values are higher than the ones obtained with JxV measurements, as previously observed [14]. The values of ideality factor and barrier height obtained by JxV measurements in this work in diodes with thick Co layers and low reverse current, of 1.19 and 0.65 eV, are close to the ones already reported in the literature [8], of n=1.04 and Φ_b=0.57, respectively, besides the fact that in this reference the author used the Richardson constant of n-type Si.

4. CONCLUSIONS

Co/p-Si Schottky diodes were prepared by photoinduced electrodeposition of cobalt on p-type silicon, with Co thickness ranging from 28 to 165 nm. The magnetic behaviour is characteristic of ferromagnetic materials, with coercivity depending on thickness. Coercivities of 50 Oe were obtained for thickness higher then 80 nm. These devices were electrically characterized by JxV and CxV measurements. The concentration of $CoSO_4$ in electrolyte does not show any significant influence on the electrical response of the diodes, since similar values were obtained for the barrier height and ideality factor. However, by reducing the Co thickness, an increase in the reverse current and ideality factor is observed, concomitant with a decrease in the barrier height.

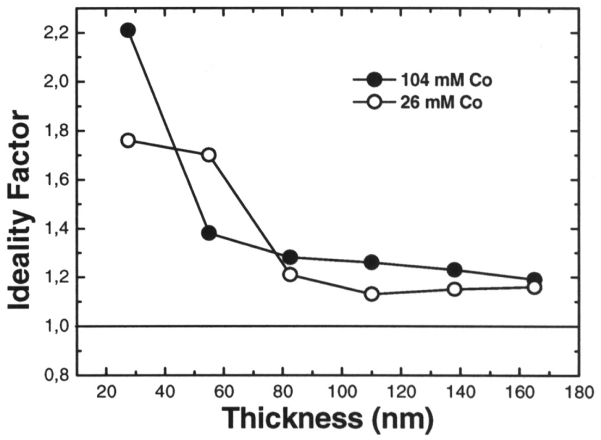

Figure 7. Ideality factor from thermionic emission theory as a function of Co thickness in electrodeposited Co/p-Si structures, for 26 and 104 mM of $CoSO_4$ in the electrolyte.

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