

Available online at www.sciencedirect.com



Surface Science 572 (2004) 337-346



www.elsevier.com/locate/susc

# Structural study of the $Ag(110)c(2 \times 2)$ -Sb phase by low energy electron diffraction

V.B. Nascimento <sup>a,\*</sup>, R. Paniago <sup>b</sup>, A. de Siervo <sup>c,d</sup>, C.M.C. de Castilho <sup>a</sup> R. Landers <sup>c,d</sup>, E.A. Soares <sup>b</sup>, V.E. de Carvalho <sup>b</sup>

<sup>a</sup> Grupo de Física de Superfícies e Materiais, Instituto de Física, Universidade Federal da Bahia, Campus da Federação, 40210-340 Salvador, BA, Brazil

<sup>b</sup> Departamento de Física, ICEx, Universidade Federal de Minas Gerais, Caixa Postal 702, 30123-970, Belo Horizonte, MG, Brazil <sup>c</sup> Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas, Caixa Postal 6165, 13083-970, Campinas, SP, Brazil <sup>d</sup> LNLS—Laboratório Nacional de Luz Síncrotron, Caixa Postal 6192, 13084-971, Campinas, SP, Brazil

Received 18 May 2004; accepted for publication 3 September 2004

#### Abstract

This work concerns the deposition of Sb on the (110) clean surface of silver. Two structured phases have been observed: an  $Ag(110)(4 \times 1)$ -Sb, with a Sb coverage of about 1.0 ML and an  $Ag(110)c(2 \times 2)$ -Sb, with half the coverage of the first one. The structural determination of the  $Ag(110)c(2 \times 2)$ -Sb phase has been performed by a standard LEED analysis and the results obtained indicate the presence of substitutional Sb atoms in the first atomic layer. The presence of the Sb substitutional atoms promotes an expansion in the first interlayer distance without any change in the surface thermal vibrational behaviour. Based on results obtained by this study and previously published ones, the substitutional site seems to be most energetically favourable for Sb atoms, in any of the low index surfaces of silver. © 2004 Published by Elsevier B.V.

Keywords: Antimony; Silver; Surface structure, morphology, roughness, and topography; Low energy electron diffraction (LEED)

#### 1. Introduction

Surfactant chemical species are defined as those atoms that, when adsorbed on specific crystal

\* Corresponding author. Tel.: +55 71 247 2033x221; fax: +55 71 235 5592.

E-mail address: von@ufba.br (V.B. Nascimento).

planes, remains at the surface, without being incorporated into the substrate during growth. This occurs with both homo- and hetero-epitaxy, inducing a layer-by-layer growth, instead of an island growth, as it would be the case without the presence of such atomic species. Sb plays the role of a surfactant in the homo-epitaxy growth of Ag on Ag(111) [1,2], changing the growth mode from

islanding to a layer-by-layer one. The effect of Sb on nucleation and growth of Ag on Ag(100) has also been studied [3] and a first principle calculation was performed [4]. The layer-by-layer behaviour of the homo-epitaxial growth of Ag(100) can be improved by the deposition of Sb on the clean surface, due to an enhancement in the interlayer transport [3]. Structural determination of the Ag(111)-Sb system has already been the object of investigation [5-7], with two ordered phases being found. The  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase structure was already determined [5-8], indicating the presence of substitutional Sb atoms in the first atomic layer. The structure of the higher Sb coverage phase, the  $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ , remains unknown [9,10]. Although two experimental ion scattering studies [5,8] indicate, for the  $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ , a structural model consisting of a  $(2 \times 2)$  Sb overlayer on the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  substitutional model [5–8], other two works associated with LEED [9] and PED [10] techniques were unable to come to a final structure for this phase, due to the obtained poor theory-experiment agreement.

To our present knowledge, there is no reference in the literature about ordered structures resulting from the deposition of Sb on the Ag(100) and Ag(110) faces. There are theoretical studies on the (100) [4] and X-ray diffraction measurements on the growth of Ag on Ag(100) with Sb [3], but no experimental evidence of a (100) ordered phase. The study of Sb deposited on an Ag(110) plane constitutes the motivation of this work. Ag(110) is the most open low index plane of silver crystal, what makes it interesting to study the possibility of intermixing adsorbed atoms that remain on the surface in other more compact planes.

Ag and Sb have atomic radii that, depending on the determination criteria, differ from each other by 10-25%. There is even not a unanimous opinion about which one is greater. The variation range goes from 1.34Å [11] till 1.75Å [12] for Ag and from 1.33Å [13,14] up to 1.75Å [15,16] for Sb. The possibility of intermixing naturally then raises the question of atomic radii. This point, in the case of Ag and Sb atoms, becomes a non-trivial question. Silver has an fcc structure while Antimony has a rhombohedral structure so, while for Ag we can define the atomic radius considering the 12fold coordination of an fcc structure, it appears to us that it would not be the most adequate for Sb. However, this is a matter of controversy. Slater [17,18] performed a careful comparison of bond lengths in ionic, metallic and covalent crystals, from which values of 1.60 and 1.45 Å are suggested for Ag and Sb, respectively. Ref. [13] presents values that range from 1.53 up to 1.65Å for Ag and from 1.33 to 1.45 Å for Sb, depending on the determination criteria. On the same direction [12] indicates an atomic radius for Ag as being 1.75 and 1.53 Å for Sb. There are, on the other hand, values for these atomic radii that do not relate with each other in the same way. Ref. [11] indicate, for Ag, covalent and atomic radii as being 1.34 and 1.44 Å, respectively while, for Sb, 1.41 and 1.61 Å. Very similar results appear in Ref. [19] while [15] indicates 1.39-1.45 for Ag and 1.64-1.69 for Sb. One reference [20] attributes equal radii for both atoms (1.45 Å). And the controversy goes on: in a recent theoretical work [21] the atomic radius of Ag is given as being 2.52 and 1.68 Å for Sb. Despite these contradictory numbers for the atomic radii, we have considered, within the muffin-tin approximation, a set of pairs for the radii, as it will be further detailed. In our view, this does not seriously affect the multiple scattering LEED calculations, under the arguments presented in Section 3.

Keeping in mind the controversy regarding the relative size of the atomic radii for Ag and Sb, it is worth to explore the possibility of formation of a structured surface layer with subsurface Sb atoms on Ag(110). This possibility, a consequence of the openness of the (110) face, is in opposition to the substitutional structure previously observed in the case of the Ag(111) face [6].

In the next section the experimental details will be discussed. The details of the theoretical LEED calculations will be presented in Section 3. A discussion of the results obtained and the final conclusions will be respectively presented in Sections 4 and 5.

#### 2. Experiment

The experiments, concerning the Sb deposition on a clean Ag(110) surface and LEED I(V) data

acquisition, were conducted in an ultra-high-vacuum chamber equipped with facilities for sample preparation (cleaning, heating and deposition) and sample characterization (Auger and XPS), as well as with a computer controlled LEED diffractrometer, at the Surface Physics Laboratory (DF-UFMG-Brazil). The silver crystal was supplied by the Monocrystal Company, with 99.995% purity, presenting a mirrorlike (110) surface oriented within  $\pm 1^{\circ}$ . The (110) silver surface was cleaned with several cycles of sputtering/annealing (Ar<sup>+</sup> ions at 1.0keV; 450°C, 30min) until no trace of carbon, oxygen and sulphur contaminations could be detected by XPS, and a sharp  $(1 \times 1)$  LEED pattern could be observed. In order to investigate the possible formation of structured phases, resulting from the deposition of Sb on an Ag(110) clean surface, a initial deposition of approximately 1.0 ML of Sb was performed, using a small e-beam cell loaded with 99.999% pure Sb, while the Ag(110) surface was kept at a temperature of 150°C. After this initial deposition, the sample was annealed to a temperature of 250 °C for 40 min and slowly cooled down to room temperature. After that, a sharp LEED pattern could be observed, indicating a  $(4 \times 1)$  reconstruction (Fig. 1a). A second annealing procedure at a higher temperature (350°C for 50min) induced a transition from the  $(4 \times 1)$  phase to a  $c(2 \times 2)$  (Fig. 1b). It was possible to compare the Sb-coverage of these two structures by using the corresponding XPS spectra, as shown in Fig. 2. From these results it is possible to verify that the peak ratio between the Sb3d signal for the  $(4 \times 1)$  and the one for the  $c(2 \times 2)$  is around 2.0. In spite of the fact that a detailed phase diagram for the Ag(110)/Sb system was not obtained, the results reported in this paper are, up to our present knowledge, the first investigation on the presence of structured phases of Sb on Ag(110), and deserves a proper investigation of their precise structures. The  $(4 \times 1)$  structure has appeared at higher coverages, but it is not yet clear if it is a meta-stable one. Despite this, it has been possible to show that it is reproducible, sometimes showing a coexistence with the centered phase, an evidence that this phase is dependent on experimental procedures, i.e., Sb coverage and annealing temperature. As a result, further specific



Fig. 1. LEED patterns at room temperature and an energy of 116eV for: (a) Ag(110)( $4 \times 1$ )–Sb phase, at a Sb coverage of about 1.0ML; (b) Ag(110) $c(2 \times 2)$ –Sb phase, at a Sb coverage of 0.5ML.



Fig. 2. XPS spectra for the  $(4 \times 1)$  and  $c(2 \times 2)$  structured phases, obtained with AlK<sub>a</sub>. From these results it is possible to verify that the Sb coverage for the  $(4 \times 1)$  phase is about twice as the one for  $c(2 \times 2)$ .

investigation is still in progress. On the other hand, the  $c(2 \times 2)$  phase was stable, giving a clear and sharp LEED pattern. LEED patterns for the  $c(2 \times 2)$  phase were recorded at an energy range

of 30-300 eV, with the sample at a temperature of 300 K, using an Omicron LEEDStar video-LEED system at a normal incidence geometry. It was not possible to extend the energy range for the collected curves due to two reasons. First, the relatively high symmetry (p2mm) observed in the experimental LEED patterns, reduces the number of independent beams at normal incidence. Second, it is necessary to consider the low Debye temperatures for Ag and Sb atoms (respectively 225 and 211K [22]). As a result, the relatively large thermal vibrations will reduce the intensity of the diffracted electrons beams and make the collection of I(V) curves at high energies very difficult, specially with the sample kept at room temperature. The LEED I(V) experimental data collected for the Ag(110) $c(2 \times 2)$ -Sb phase comprises a total energy range of 888 eV (seven independent beams), what appears to be a reasonable energy range for room temperature LEED I(V) measurements.

Curves of the intensity versus voltage were extracted from the digitized diffraction patterns for 7 fractional beams  $\left[(\frac{1}{2},\frac{1}{2}),(\frac{1}{2},0)\right].$ 

#### 3. Theoretical details

A standard LEED structural determination approach for the theoretical calculation of the I(V) curves was adopted. The potential calculation was done using the muffin-tin model, and the Barbieri/Van Hove Phase Shift code [23] was used in the calculation of the muffin-tin potentials and phase shifts for the Ag and Sb atoms. The atomic orbitals for each element were obtained by a self-consistent calculation within the Dirac-Fock approach. Matteis' prescription was adopted in the calculation of the muffin-tin potential and the rel-

ativistic phase shifts were evaluated by numerical integration of the Dirac equation.

Muffin-tin different radii were adopted for the Sb and Ag atoms, accordingly to the different values available in the literature, with nine phase shifts being employed in the calculations. The adopted values for each case, just define the radii of the muffin-tin potential for both atoms. The atomic scattering is described by the atomic phase shifts, that are very sensitive to the slope of the muffin-tin potential curve (which is responsible for the atomic scattering "information") but not to the muffin-tin radius [24]. The adopted muffintin different radii have a negligible effect in the phase shifts determination, at least in the considered variation range, since the potential varies very slowly with the distance from the nucleus, presenting an almost constant value. Changes only would occur in the so called muffin-tin zero, the constant potential among the muffin-tin spheres [24]. This constant potential, is related to the constant part of the so called "inner potential" [25], and this one is optimized during the structural search process, minimizing the effects of variations in atomic radii. The same argument applies to the Ag atom. Also, in the multiple scattering calculations, the phase shifts fully describe the atomic scattering, and the atoms are treated as point scatterers, without any dimension. So, no significative change was observed in the final structural model results, as shown in the next section.

A set of parameters was assumed in the calculations, such as temperature of 300 K, normal incidence and a bulk Debye temperature of 225 K. For the real and imaginary parts of the optical potential, the values of  $V_0 = 10.0 \text{ eV}$  and  $V_{0I} = -4.0 \text{ eV}$  were adopted, and the real part fitted during the optimization process.

Full dynamic LEED calculations were performed on an AMD-Athlon 1.3 GHz personal computer, running Linux Operational System, and using the symmetrized automated tensor LEED (SATLEED) [23] code. Six different and symmetrically acceptable structural models were then investigated for the  $Ag(110)c(2 \times 2)$ –Sb, with the Sb atoms occupying different adsorption sites: on top (model A), short-bridge (model B), longbridge (model D), centered (model C) and substi-

tutional sites in the first (model E) and second (model F) atomic layers. These models are schematically presented in Fig. 3. As inferred from the experimental data, all models present an Sb coverage of 0.5 ML and a p2mm symmetry.

In the search for the structure for which the calculated I(V) curves best resembles the experimental ones, the reliability-factor (R-factor), as defined by Pendry [26], was employed. The optimization procedure was performed using a mix of search methods:

In this first step, only the atomic vertical coordinates (normal to the (110) surface) of the atoms in the first and second layers were optimized, for each one of the six investigated structural models. This restriction comes from the necessity of keeping the *p2mm* symmetry, what was experimentally observed as being the case. The Powell Directed Search method [27] (one of the search engines available in the SATLEED code [23]) was used in this optimization step, aiming to choose the model that presented the

best theory-experiment agreement. The R-factor values, calculated for the six models are shown in Table 1. It is clear that models C, E and F resulted in R-factors values clearly better than the other models.

- 2. The Debye temperatures of the first two atomic layers of the three models with better  $R_P$  (C, E and F models), as determined in the previous step, were optimized, in this second step, using a grid search procedure. The vertical coordinates of the atoms were kept in their optimum positions (as found in the first optimization step) during the temperature grid search.
- 3. In order to perform a final refinement of the structure, another optimization of the vertical coordinates was executed, using the Powell Directed Search algorithm, but, this time, the optimum values of the Debye temperatures for the first two atomic layers found in step 2 were used. The final structure for the Ag(110) $c(2 \times 2)$ -Sb was then obtained as being the one resulting from this refinement procedure.



Fig. 3. Structural models proposed for the  $Ag(110)c(2 \times 2)$ -Sb phase: (A) on-top site, (B) short-bridged site, (C) centered site, (D) long-bridged site, (E) first-layer substitutional site and (F) second-layer substitutional site.

V.B. Nascimento et al. | Surface Science 572 (2004) 337-346

Table 1

 $Ag(110)c(2 \times 2)$ -Sb:  $R_P$  values obtained for each of the proposed models, in the initial structural optimization (step 1)

Model	Final R <sub>I</sub>
Model A: on top site	0.55
Model B: short-bridged site	0.54
Model C: centered site	0.33
Model D: long-bridged site	0.49
Model E: substitutional site—1st layer	0.24
Model F: substitutional site-2nd layer	0.37

As it can be inferred by the low  $R_P$  obtained, models C, E and F appear to be the most plausible structures among the six initially proposed.

In the next section we will present a detailed discussion of the results obtained in each step of the optimization process as described above.

#### 4. Results and discussion

As previously mentioned, in the first step of the search process, the vertical coordinates of the Ag and Sb atoms for each one of the six proposed structural models for the  $c(2 \times 2)$  phase, were optimized using the Powell Directed Search algorithm. There is no reason for exploring variation of the in-plane coordinates (parallel to the surface) since this would cause loss of symmetry. Only three structural parameters were optimized for every model, except for model A (on top site) where four parameters were investigated. The resulting  $R_{\rm P}$  values obtained for each model are presented in Table 1. As it can be inferred from these results, models C, E and F can, in principle, be considered as the most plausible ones, deserving a closer investigation.

In the next optimization step, the Debye temperatures for the first layer, containing Ag and Sb atoms,  $(\Theta_{D1})$ , and second layer, this one just with Ag atoms  $(\Theta_{D2})$ , in models C, E and F, were optimized employing a grid search method. The values for the vertical coordinates of the first two atomic layers were kept fixed at their optimum results, obtained in the previous step, during this part of the search procedure. The R-factors values obtained for models C, E and F, after this search step, were, respectively, equal to 0.31, 0.19 and



Fig. 4.  $R_P$  surface obtained with the optimization of the Debye temperatures of the first ( $\Theta_{D1}$ -Ag and Sb atoms) and second ( $\Theta_{D2}$ -Ag atoms) layers for the best  $R_P$  model (model E). A well defined minimum can be observed for  $\Theta_{D1} = 160$  K and  $\Theta_{D2} = 170$  K.

0.29, indicating model E as the best option for an additional refinement. The results obtained in the grid optimization of  $\Theta_{D1}$  and  $\Theta_{D2}$ , for model E, are presented in Fig. 4, where the  $R_{\rm P}(\Theta_{\rm D1}, \Theta_{\rm D2})$ surface can be seen, indicating a well defined minimum at  $\Theta_{D1} = 160$  K and  $\Theta_{D2} = 170$  K. These values are in good agreement with experimental results for Ag(110) clean at a temperature of 323 K [28], that indicates  $\Theta_{D1} = 160$  K and  $\Theta_{D2}$  = 170 K. So, the presence of Sb substitutional atoms in the first atomic layer seems not to affect the Ag(110) surface thermal vibrations. It is also possible to observe that the search process by varying the Debye temperature results in a pronounced variation in R-factor (from 0.24 to 0.19 in model E). This does not occur for more compact surfaces as, for example, the Ag(111)( $\sqrt{3} \times \sqrt{3}$ ) surface [6]. It seems to be reasonable, since the (110) fcc face is more open than the (111).

The final step consisted in a refinement of the structural parameters for model E, using the Powell Directed Search algorithm. The optimum  $\Theta_{D1}$  and  $\Theta_{D2}$  values, previously obtained, were

342

adopted in these final calculations. A good theoryexperiment agreement was obtained after the optimization process, as it can be implied by the final  $R_P$  value of 0.19. A comparison between theoretical and experimental I(V) curves can be done by observing the curves presented in Fig. 5. The final results obtained for each investigated pairs of Sb and Ag radii are presented in Table 2. As can be seen there, the final  $R_P$  obtained values present a negligible variation, that is within the associated error. The optimum values for the optimized structural and non-structural parameters, essentially the same in all the explored cases, are presented in Table 3 and the Ag(110) $c(2 \times 2)$ –Sb phase final structure can be seen in Fig. 6.

In associating the real structure with the one corresponding to model E, some considerations can be done. The behaviour of the first interlayer distance  $d_{12}$ , as compared with the bulk one, is similar to what occurs with the (111) face [6,7,29], in the case of the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase. The presence of Sb substitutional atoms in the first atomic layer has caused, for both (111) and (110) faces, an expansion of the first inter-layer distance.

Table 2

Model E: final $R_{\rm P}$ values for each	investigated pair of muffi	n-tin
radii for Ag and Sb atoms		

0				
Sb radius (Å)	Ag radius (Å)	Final $R_{\rm P}$	Reference	
1.45	1.60	$(0.191 \pm 0.040)$	[13]	
1.45	1.45	$(0.192 \pm 0.040)$	[20]	
1.59	1.44	$(0.192 \pm 0.040)$	[19]	
1.64	1.45	$(0.194 \pm 0.040)$	[15]	
1.75	1.44	$(0.194 \pm 0.040)$	[15,16]	

In Ag(111)( $\sqrt{3} \times \sqrt{3}$ )R30°–Sb the presence of Sb increases  $d_{12}$  by  $\approx 4\%$ , in comparison with the Ag(111) clean, which does not relax (bulk termination). In the clean Ag(110) face, there is a contraction in the first inter-layer distance ( $d_{12}$ ) of 7.8% (at 323 K [28]), compared to bulk value, while in the Ag(110) $c(2 \times 2)$ –Sb this contraction is reduced to 5.3%. Thus, these results suggest that the presence of Sb causes a variation of  $d_{12}$  in the same direction for either face (111) or face (110). It is important to emphasize that this expansion in the first interlayer distance of Ag(110), with the presence of substitutional Sb,



Fig. 5. Experimentally collected and best-fit theoretical I(V) curves for the Ag(110) $c(2 \times 2)$ -Sb phase. Individual  $R_P$  values for each beam are also indicated.

344

Table 3 Model E—final structure: best values for the optimized structural and non-structural parameters

······ · · · · · · · · · · · · · · · ·		
Parameter	Final value	
$\Delta Z_{AgSb}(rumple)$	$(\downarrow 0.05 \pm 0.05)$ Å $(\downarrow 4.2\%)$	
$d_{12} (\Delta d_{12})$	$(1.37 \pm 0.04)$ Å $(-5.3\%)$	
$d_{23} (\Delta d_{23})$	$(1.48 \pm 0.04)$ Å (+2.5%)	
$d_{\rm BULK}$	1.4443 Å	
$\Theta_{\mathrm{D1}}$	$(160 \pm 60) \mathrm{K}$	
$\Theta_{\mathrm{D2}}$	$(170 \pm 100) \mathrm{K}$	
$\Theta_{\mathrm{DBULK}}$	225 K	
Final R <sub>P</sub>	0.19	

 $\Delta Z_{AgSb}$ ,  $d_{12}$ ,  $d_{23}$  and  $d_{BULK}$  are assigned to the Ag–Sb rumpling in the first layer (see Fig. 6), first, second an bulk interlayer distances respectively.  $\Delta d_{12}$  and  $\Delta d_{23}$  correspond to the percentual variation in the first and second interlayer distances regarding bulk termination interlayer value. The rumple  $\Delta Z_{AgSb}$  is also presented as a percentual value concerning bulk value and the  $\downarrow$  sign stands for a negative rumple, i.e., the Sb atoms are on the bottom of the first atomic layer. The Debye temperatures for the first, second and bulk layers are represented by  $\Theta_{D1}$ ,  $\Theta_{D2}$  and  $\Theta_{DBULK}$  respectively.

does not produce any effect in the first two atomic layers thermal vibrations, as previously discussed.

Another aspect, for which is possible to establish a comparison between (111) and (110) faces, concerns with the substitutional character of the deposited Sb atoms. As considered in this work, the atomic radius of Sb was assumed, as a result of differences in the literature for the atomic radii, as being smaller, greater and even equal to the one of Ag. Despite the fact that the face (110) of silver, among the ones with small indexes, is the most open, this does not result in a sub-surface structure as could, in principle, be expected, at least if Sb has a smaller radius than Ag. There are, however, arguments on the opposite direction. What, perhaps, is important here is that, for LEED calculations, we need the muffin-tin radius, a concept that not necessarily matches the concept of atomic radius. As shown, the structural results are not sensitive to small variations in the muffin-tin radii. What can be inferred from this fact-equally observed for the (111) surface—is that the substitutional position for Sb on Ag is energetically more favourable. Two theoretical calculations carried out by Woodruff and Robinson [29] and Jiang and co-workers [4] has lead to the same conclusion for the (111) and (100) surfaces.

Concerning the distance between the planes defined by atoms of Sb or Ag (rumple) in the first layer, denoted here by  $\Delta Z_{AgSb}$ , the obtained experimental value indicates that there is no rumple, at least within the associated error. This result would be consistent with the possibility of antimony



Fig. 6. The Ag(110) $c(2 \times 2)$ -Sb structure side view. Black and white spheres are assigned to Sb and Ag atoms respectively.  $\Delta Z_{AgSb}$ ,  $d_{12}$  and  $d_{23}$  stand respectively for the Ag-Sb first layer rumple, first and second interlayer distances.

atoms having a smaller, or even equal radius, when compared with the silver ones. However, the same was observed for calculations performed for Ag atoms being smaller than the Sb ones. In this last approach, i.e. assuming the antimony atom to be the larger one, e.g., atomic radii of 1.44 and 1.59Å for Ag and Sb respectively [19], a simple hard sphere approximation would lead to a rumple of 0.94 Å. However, these considerations are under the constraints of peculiar surface effects which could lead to a change in the effective atomic radii at surfaces [30,31]. If we compare the rumple amplitude obtained by LEED for the (111) [6] and (110) surfaces (this work) we can observe a trend, previously suggested, for the rumple amplitude to decrease with decreasing atomic density of the surface layer [32]. Values of  $(0.07 \pm 0.04)$  A [6] and  $(-0.05 \pm 0.05)$ Å have been obtained for the rumpling amplitude of the closest (111) and most open (110) silver surfaces, suggesting, within the error constraints, a larger rumple for the (111) surface. This result seems to be in agreement with recently published works concerning the structural determination of phases obtained with the deposition of Sn on the (111) [32] and (110) [33] surfaces of Ni.

#### 5. Conclusions

This work has shown the existence of two ordered phases for Sb deposited on Ag(110):  $Ag(110)(4 \times 1)$ -Sb and a  $Ag(110)c(2 \times 2)$ -Sb. It was possible, using the LEED experimental technique, to determine the structure of the centered phase, with a value of 0.19 for the Pendry R-factor, a result that gives reason to believe on the correctness of the structure. At this surface, similarly to what occurs with the Ag(111)( $\sqrt{3} \times \sqrt{3}$ )R30° system, the comparison between experimental and theoretical curves has shown that the Sb atoms occupy substitutional positions, instead of forming a subsurface structure, as could be expected considering the characteristic openness of the (110) fcc face and the relative size of the atomic radii for Ag and Sb. The rumple of the Sb atoms, in comparison to the Ag ones, is negligible or non-existent within the error limitation, less

than the one observed in the case of the (111) face. This is consistent with previous considerations by Woodruff and Robinson [31], accordingly to "the reduced rumple is a true surface effect". Another point which, at least in the present case, confirms this argument, is that the final optimized structure has shown to be insensitive to small variations on the muffin-tin radii. When comparing the clean Ag(110) and the Ag(110) $c(2 \times 2)$ –Sb, it is possible to observe that the presence of Sb reduces the first to second layer interplanar distance from -7.8% (at 323 K [28]) to -5.3%, without modifying the vibrational behaviour of the two first layers.

#### Acknowledgments

The authors acknowledge the financial support of CNPq, CAPES, FAPESB, FAPEMIG and FAPESP, Brazilian agencies, and LNLS where early measurements that motivated this work were carried out. This work has partial support of FI-NEP-CTPETRO/FAPEX/UFBA (contract 65.99.0487.00). The authors also would like to acknowledge the experimental collaboration of Mr. M.F. Carazolle and the text revision done by Ms. A.C.F. de Castilho.

#### References

- H.A. van der Vegt, H.M. van Pinxteren, M. Lohmeier, E. Vlieg, J.M.C. Thornton, Phys. Rev. Lett. 68 (1992) 3335.
- [2] J. Vrijmoeth, H.A. van der Vegt, J.A. Meyer, E. Vlieg, R.J. Behm, Phys. Rev. Lett. 72 (1994) 3843.
- [3] H.A. van der Vegt, W.J. Huisman, P.B. Howes, E. Vlieg, Surf. Sci. 330 (1995) 101.
- [4] M. Jiang, X. Zhou, M. Qiu, P. Cao, J. Phys.: Condens. Matter 10 (1998) 8653.
- [5] T.C.Q. Noakes, D.A. Hutt, C.F. McConville, D.P. Woodruff, Surf. Sci. 372 (1997) 117.
- [6] E.A. Soares, C. Bittencourt, V.B. Nascimento, V.E. de Carvalho, C.M.C. de Castilho, C.F. McConville, A.V. de Carvalho, D.P. Woodruff, Phys. Rev. B 61 (2000) 13983.
- [7] S.A. de Vries, W.J. Huisman, P. Goedtkindt, M.J. Zwanenburg, S.L. Bennet, I.K. Robinson, E. Vlieg, Surf. Sci. 414 (1998) 159.
- [8] P.D. Quinn, D. Brown, D.P. Woodruff, P. Bailey, T.C.Q. Noakes, Surf. Sci. 511 (2002) 43.
- [9] V.B. Nascimento, Dr. Thesis, Universidade Federal de Minas Gerais, Brazil (in Portuguese).

346

V.B. Nascimento et al. | Surface Science 572 (2004) 337-346

- [10] E.A. Soares, A. de Siervo, R. Landers, Universidade Estadual de Campinas—UNICAMP (private communication).
- [11] http://www.qivx.com/ispt/elements/ptw\_047.php, http:// www.qivx.com/ispt/elements/ptw\_051.php.
- [12] http://www.lasurface.com/xps/Periodiq\_table/ A\_new\_pergen2.htm.
- [13] http://www.webelements.com.
- [14] E. Clementi, D.L. Raimondi, W.P. Reinhardt, J. Chem. Phys. 38 (1963) 2686.
- [15] C.T. Campbell, Surf. Sci. 167 (1986) L181.
- [16] W.H. Zachariasen, J. Inorg. Nucl. Chem. 35 (1973) 3487.
- [17] J.C. Slater, J. Chem. Phys. 39 (1964) 3199.
- [18] J.C. Slater, Quantum Theory of Molecules and Solids, McGraw-Hill, New York, 1965.
- [19] http://web.mit.edu/3.091/www/pt/pert1.html.
- [20] http://www.science.uwaterloo.ca/cchieh/cact/tools/ elemprop.html.
- [21] D.C. Ghosh, R. Biswas, Int. J. Mol. Sci. 3 (2002) 87.
- [22] C. Kittel, Introduction to Solid State Physics, sixth ed., John Wiley & Sons, New York, 1986.
- [23] A. Barbieri, M.A. Van Hove (private communication); http://electron.lbl.gov/leedpack/.

- [24] T. Loucks, Augmented Plane Wave Method, Benjamin, New York, 1976.
- [25] M.A. Van Hove, W.H. Weinberg, C.-M. Chan, Low Energy Electron Diffraction—Experiment, Theory and Surface Structure Determination, Springer, Berlin, 1986.
- [26] J.B. Pendry, J. Phys. C 13 (1980) 937.
- [27] W.H. Press, B.P. Flannery, S.A. Teukolsky, W.T. Vetterling, Numerical Recipes in Fortran, Cambridge Univ. Press, Cambridge, 1989.
- [28] V.B. Nascimento, E.A. Soares, V.E. de Carvalho, E.L. Lopes, R. Paniago, C.M.C. de Castilho, Phys. Rev. B 68 (2003) 245408.
- [29] D.P. Woodruff, J. Robinson, J. Phys.: Condens. Matter 12 (2000) 7699.
- [30] D. Brown, P.D. Quinn, D.P. Woodruff, Phys. Rev. B 61 (2000) 7706.
- [31] D.P. Woodruff, J. Robinson, Surf. Sci. 219 (2003) 1.
- [32] E.A. Soares, C. Bittencourt, E.L. Lopes, V.E. de Carvalho, D.P. Woodruff, Surf. Sci. 550 (2004) 127.
- [33] P.D. Quinn, C. Bittencourt, D. Brown, D.P. Woodruff, T.C.Q. Noakes, P. Bailey, J. Phys.: Condens. Matter 14 (2002) 665.