



High-temperature Auger electron spectroscopy of Zircaloy-4

N. Stojilovic, E.T. Bender, R.D. Ramsier*

Departments of Physics, Chemistry, and Chemical Engineering, The University of Akron, Akron, OH 44325-4001, USA

Received 4 November 2004; accepted 18 March 2005

Available online 9 April 2005

Abstract

The near-surface region of Zircaloy-4 (Zry-4) has been probed using Auger electron spectroscopy (AES). In particular, the behavior of impurity (sulfur) and alloying (tin) elements has been monitored as a function of annealing temperature and time. High-temperature AES experiments above 900 K are reported, with a primary focus on changes in the S(LMM) Auger feature that overlaps with the primary Zr(MNV) transition. We find that the sulfur content of the near-surface region increases linearly with annealing time at higher temperatures. Tin is the only alloying element whose Auger signal intensity significantly exceeds the noise level at these temperatures.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Zircaloy-4; Sulfur; Tin; Auger electron spectroscopy; Annealing

1. Introduction

Zircaloy-4 (Zry-4) is known as structural material of choice in harsh environments like water-cooled nuclear reactors, where its combination of exceptional corrosion resistance, low thermal neutron absorption cross-section, and good material strength are essential. Studies dealing with this alloy and its nuclear applications are usually focused on corrosion [1–3], oxidation [4–11], or hydrogen absorption kinetics [12–14]. We are mainly interested in understanding how this material behaves at higher temperatures, where diffusion of impurities and alloying elements

into or out of the bulk may alter its surface chemistry. With this article we initiate our research efforts on the surface chemistry on Zry-4 under ultra-high vacuum conditions. Our results will provide a basis for comparison to our previous work on the surface chemistry of single crystal zirconium surfaces [15–18]. Such comparisons should be relevant from both the applied and fundamental point of view.

Removing impurities from the surface and subsurface regions of zirconium and its alloys has always been a challenge. Cleaning zirconium is exceptionally difficult since high-temperature annealing of zirconium-based materials results in the dissolution of surface oxygen and carbon atoms but, on the other hand, induces sulfur segregation toward the surface region. However, due to overlapping Zr(MNV) and S(LMM) Auger features, it is difficult to monitor

* Corresponding author. Tel.: +1 330 972 4936;

fax: +1 330 972 6918.

E-mail address: rex@uakron.edu (R.D. Ramsier).

sulfur segregation by Auger electron spectroscopy (AES). As a consequence, there are inconsistencies in the literature concerning AES data and the cleanliness of zirconium surfaces [19–25]. These inconsistencies are inferred from the relative intensities of the Zr(MNV) + S(LMM) and Zr(MNN) AES features. This paper addresses this issue by monitoring AES intensities as a function of annealing time and temperature, with the goal of investigating surface segregation before we proceed with molecular-adsorption experiments.

2. Experimental details

The stainless steel ultra-high vacuum system used in this study was described elsewhere [26,27]. During experiments, we employed ion getter and titanium sublimation pumps, whereas the turbo-molecular pump was used during cleaning of the sample by 2 keV Ar-ion sputtering. The cleaning procedure consisted of sputtering (Ar, 99.9999%, Matheson), followed by annealing at different temperatures at which AES experiments were performed. The base pressure during experiments was $\sim 4 \times 10^{-10}$ Torr. The newly mounted Zry-4 sample, cut from sheet stock provided by Wah Chang, had a surface area of 0.53 cm^2 and a thickness of 2 mm. The sample was mechanically polished to a mirror-like finish with successively finer diamond pastes, and finally with a $0.05 \text{ }\mu\text{m}$ alumina suspension. After polishing, the sample was sonicated for 20 min in a solution of Micro-90 (International Products Corp.), and then in acetone. The elemental composition of Zry-4 is nominally, in wt%, 1.2% Sn, 0.2% Fe, 0.2% Cr + O + Si, and the balance Zr.

Tantalum wires, spot-welded to the sample, are used for dc heating. Two type-E thermocouples, also spot-welded to the sample, are part of a temperature-control feedback loop. Sample cooling is performed by means of a copper braid connected to a liquid-nitrogen cold finger. Four-grid retarding-field AES with an electron beam energy of 3 keV was used. In these experiments, we observe that the electron beam used for AES raises the temperature of the sample $\sim 20 \text{ K}$ at 150 K, while for experiments at 1012 K no change in the sample temperature occurs.

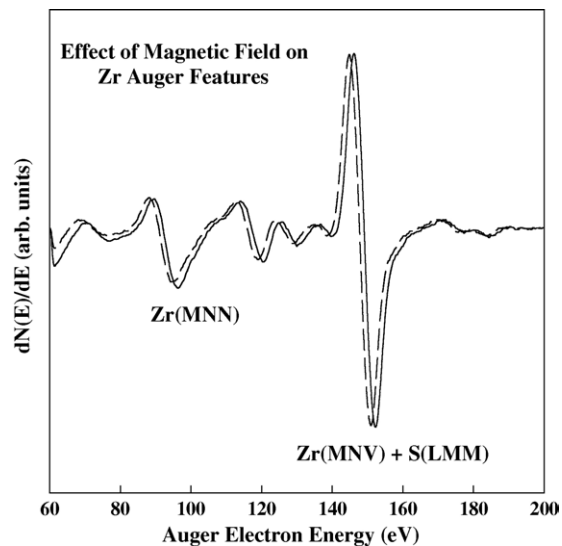


Fig. 1. Zirconium Auger electron spectra taken during annealing at 990 K (dashed line) and after the heating current was stopped (solid line). The spectrum taken during annealing (dashed line) was collected after 240 min of annealing. The magnetic field only shifts the spectrum to lower kinetic energies by 1–2 eV, but does not alter peak intensities.

In order to perform high-temperature AES experiments it is necessary to determine the effect of magnetic fields, induced by heating currents, on Auger electron spectra.

Fig. 1 shows derivative mode Auger electron spectra of zirconium features, taken after 240 min of annealing at 990 K (dashed line), and upon stopping the heating current (solid line). The latter Auger spectrum was acquired during cooling from ~ 480 to 420 K. The figure indicates the effect of magnetic fields, produced by the 40 A current flowing through the sample holder, on zirconium AES features. The magnetic field shifts the zirconium features by about 1–2 eV, but does not affect the peak heights significantly. This has been reproduced at different temperatures and verifies that we can rely on Auger peak-to-peak heights even while heating the sample.

An advantage of high-temperature AES experiments is the fact that the sticking coefficient of background gases (H_2O , H_2 , CO) is significantly reduced. Also, adsorption at these temperatures would quickly lead to dissolution of the adsorbed impurity atoms into the bulk as well. Consistently, we observe no increase in oxygen or carbon AES signals even

after several hours of exposure of the Zry-4 sample to the AES beam at high temperatures. Since rapid desorption of bulk hydrogen occurs at these temperatures [25,28], contamination of the surface with H_2 background gas is also unlikely. However, we find that several hours of AES scanning of the Zry-4 surface at room temperature results in an increase of the C(KLL) and O(KLL) features, as a result of adsorption of background gases, consistent with what was observed on Zr(0 0 0 1) [29].

3. Results and discussion

Zirconium has a very high affinity for holding impurity atoms. It is, therefore, a challenge to keep its near-surface region free from impurities even under ultra-high vacuum conditions. The major difficulty is that at higher annealing temperatures, oxygen and carbon diffuse into the bulk but sulfur segregates from the bulk into the near-surface region. Fig. 2 shows, within the detection limit of our spectrometer, what appears to be an impurity-free surface of Zry-4. Even though the surface appears to be clean, a significant amount of sulfur resides in the near-surface region, which is reflected in the Zr(MNV) + S(LMM) peak

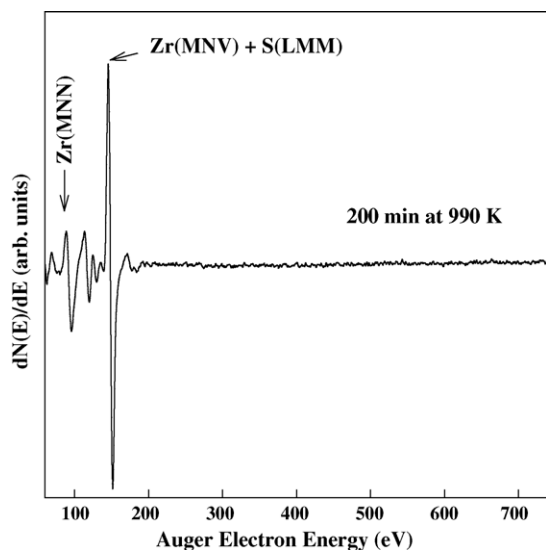


Fig. 2. Auger electron spectrum of Zry-4, taken at 990 K after 200 min of annealing at this temperature. No carbon or oxygen Auger signals are observed after prolonged annealing at 990 K, and the surface appears “clean”.

height, compared to other zirconium Auger features. It is difficult to say, based on AES results only, whether sulfur is present on the surface or in the subsurface region that is also probed by AES. The reader is referred to reference [30] for a study incorporating quantitative analysis of sulfur-segregated zirconium surfaces using depth profiling and AES. In the present study, we take a different approach, and investigate the segregation of sulfur as a function of annealing time and temperature, on a zirconium alloy. The present study is relevant to cleaning procedures used in vacuum-based studies of materials used in industrial applications.

Fig. 3 presents a series of Auger spectra obtained at ~ 145 K after sputtering (A) and during 1012 K annealing for various times (B)–(D). Note that sputtering without annealing (A) leaves some carbon and oxygen in the near-surface region. The measured Auger peak-to-peak height ratios are

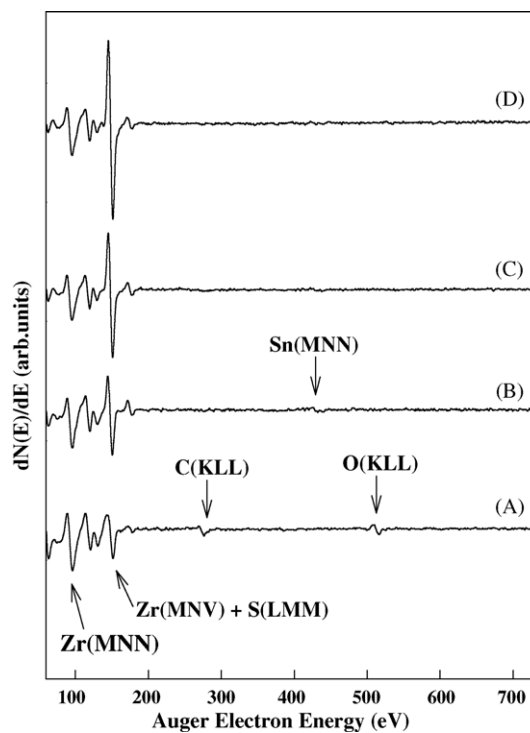


Fig. 3. A series of Auger electron spectra taken after sputtering when no annealing has been done (A), and after annealing at 1012 K for various times: 0 min (B), 80 min (C), and 180 min (D). Spectrum (A) was collected at ~ 145 K, whereas as all other spectra were taken during annealing. Each spectrum took about 7 min to acquire.

$C(KLL)/Zr(MNN) = 0.17$ and $O(KLL)/Zr(MNN) = 0.17$. Note that the $Zr(MNV) + S(LMM)$ Auger peak intensity is smaller than that of $Zr(MNN)$. Upon reaching 1012 K, carbon and oxygen are dissolved into the bulk. Spectrum (B), taken immediately upon reaching 1012 K, shows an increase in the $Zr(MNV) + S(LMM)$ Auger feature, which is now greater than the $Zr(MNN)$ peak.

The dissolution of oxygen and carbon into the bulk will result in reduced attenuation of ejected Auger electrons. However, the decrease of the $Zr(MNN)$ feature height seen by comparing spectra (A) and (B) in Fig. 3 is presumably due to partial attenuation caused by sulfur segregation which would also contribute to the increase in the $Zr(MNV) + S(LMM)$ signal. Subsequent spectra taken after further annealing, (C) and (D), reflect sulfur segregation to the subsurface or surface region. Tin $Sn(MNN)$ Auger features, present in spectrum (B) ($Sn(MNN)/Zr(MNN) = 0.09$), disappear and we observe an increase in the $Zr(MNV) + S(LMM)$ feature as a function annealing time.

In a previous study, ion scattering spectroscopy (ISS) [22] showed no evidence of sulfur in the surface layer of polycrystalline Zr for even greater $Zr(MNV) + S(LMM)$ Auger features, as compared to the $Zr(MNN)$ peak that we show in spectrum (C) of Fig. 3. Since ISS can determine only surface composition, whereas AES also probes the subsurface region, we propose that in our spectra sulfur resides in the subsurface region. Since sulfur is known to have a large AES cross-section [30], it is likely that even small quantities of subsurface sulfur are detectable in AES, through the increase in the $Zr(MNV) + S(LMM)$ feature.

There are inconsistencies regarding AES data in the literature about which feature, the $Zr(MNV)$ or the $Zr(MNN)$, is more sensitive to chemisorption. One group has claimed that the degree of attenuation increases with kinetic energy, implying that the $Zr(MNV)$ Auger feature is more sensitive with respect to chemisorption than the $Zr(MNN)$ transition [25]. On the other hand, other groups have reported that the $Zr(MNN)$ feature is effected more by adsorbates [29] and is the most surface sensitive [31]. Continuous dissolution of impurities (O, C) into the bulk at high temperatures should result in an increase in all Zr AES features based on electron scattering arguments. However, our data of Fig. 3 indicate that at high

temperatures, annealing causes the $Zr(MNN)$ Auger peak-to-peak height to decrease (compare spectra (A) and (B)), and then remain essentially unchanged (compare spectra (C) and (D)) within experimental uncertainty. However, the $Zr(MNV) + S(LMM)$ feature continues to increase, and we conclude that these changes result from sulfur segregation into the near-surface region.

Fig. 4 shows $[Zr(MNV) + S(LMM)]/Zr(MNN)$ ratios as a function of annealing time at three different temperatures. The heating rate was 1.8 K/s before the sample reached the set point temperatures. In all three cases, spectra were collected during annealing. By increasing the annealing temperature between 920 and 1012 K the diffusion rate increases. However, note that there is little difference in sulfur content after the temperature initially reaches 920, 970, or 1012 K. These initial values are close to that for sulfur-free surfaces reported by Wong and Mitchell [24] and also by Foord et al. [25]. However, from previous work on sulfur impurities in zirconium [30], it is not clear how sulfur segregation depends on annealing time. Here, as Fig. 4 indicates, above 900 K the amount of sulfur diffusing outward at three different temperatures appears to be a linear function of time. Since the $Zr(MNV)$ and $S(LMM)$ transitions overlap it is difficult to determine the exact sulfur concentration,

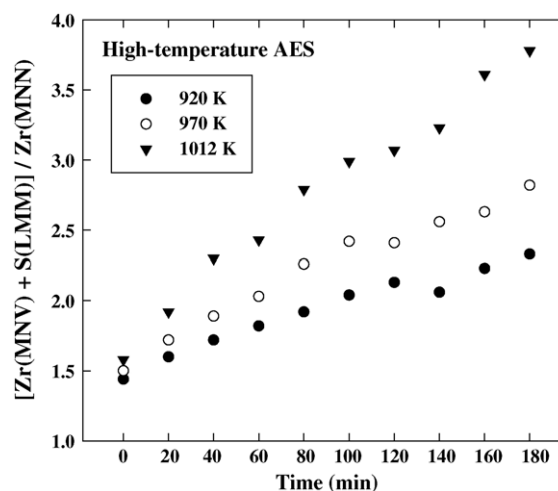


Fig. 4. The $[Zr(MNV) + S(LMM)]/Zr(MNN)$ Auger peak-to-peak height ratio as a function of annealing time. The spectra were collected during annealing at 920 K (●), 970 K (○), and 1012 K (▼).

and we make no attempt to determine quantitative diffusion coefficients from our AES experiments.

For the data sets of Fig. 4 the Zr(MNN) feature (the denominator of the plotted ratio) is essentially constant (within a few %). This implies that not only the ratio, but also the Zr(MNV) + S(LMM) feature itself, increases linearly as a function of time at these three temperatures. One may expect that sulfur segregation would result in electron attenuation effects that would be reflected in the decrease of Zr Auger signals, which we do not observe for Zr(MNN). This leads us to propose that the Zr(MNV) feature is not significantly attenuated either, and that Fig. 4 is primarily indicative of sulfur segregation into the subsurface region. This interpretation would be consistent with previous secondary ion mass spectrometry (SIMS) experiments on Zr(0 0 0 1) [32], where sulfur was not detected on the surface after high-temperature annealing.

With respect to tin, the major alloying element of Zry-4, we observe that initial annealing above 900 K results in the appearance of the Sn(MNN) feature (see spectrum (B) of Fig. 3). This may be a result of tin segregation to the surface, or reduced attenuation effects caused by oxygen and carbon diffusion into the bulk. However, prolonged annealing at 990 K or above reduces the Sn(MNN) feature to the detection limit of our AES system. Fig. 5 shows how the tin concentration in the near-surface region changes with annealing time at 990 K. Since with prolonged annealing sulfur segregates to the near-surface region, it is difficult to say exactly whether the Sn(MNN) Auger signal is reduced due to outward sulfur segregation, dissolution of tin into the alloy, or both. The intensity of the Sn(MNN) Auger signal is always relatively small, and at the temperatures studied here the Sn(MNN)/Zr(MNN) ratio was found to be 0.12 or lower. We also observe that Ar-ion sputtering for 60 min removes the tin AES signature.

Ultra-high vacuum studies of zirconium surfaces often employ annealing at temperatures at or above 900 K [22,25,30,33,34]. It is, therefore, of interest to investigate the behavior of impurity and alloying elements at these temperatures as a function of time, especially if segregation phenomena have the ability to alter subsequent molecular adsorption experiments. For example, the presence of sulfur in the surface or near-surface region is known to reduce the sticking coefficient of oxygen and to delay the oxidation of

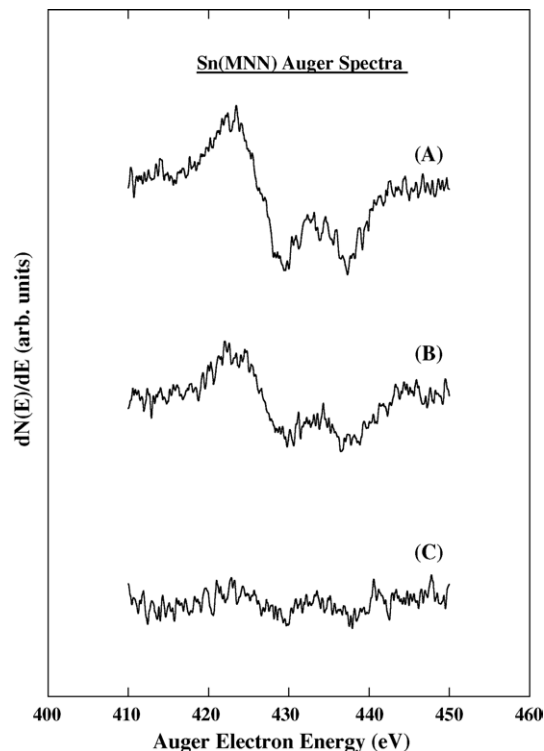


Fig. 5. The Sn(MNN) Auger feature recorded upon reaching 990 K (A), after 70 min annealing at the same temperature (B), and after 150 min of annealing (C). Prolonged annealing results in sulfur segregation toward the surface and a decrease in the AES signature of tin.

zirconium [24,30,34]. We have demonstrated that above 900 K the amount of segregated sulfur is roughly a linear function of annealing time, and propose that a $[\text{Zr}(\text{MNV}) + \text{S}(\text{LMM})]/\text{Zr}(\text{MNN})$ ratio above ~ 1.5 indicates the presence of sulfur, at least in the subsurface region, consistent with observations in reference [25]. Here, we have studied Zry-4 instead of pure zirconium, and have shown that detecting even the major alloying element with AES depends on the annealing history of the sample. This memory effect may play a role in determining the subsequent surface chemistry of Zry-4, which is a subject of on-going investigations.

4. Conclusions

Since magnetic fields produced by passing current through the sample had little effect on Auger peak-to-

peak heights, high-temperature AES has been used to probe the near-surface region of Zry-4. The advantage of high-temperature measurements is the reduced sticking coefficient of residual gas molecules so that prolonged experiments can be performed without contaminating the near surface region with carbon and/or oxygen significantly. This is particularly convenient for tracking sulfur segregation as a function of time, when the near-surface region is free from carbon and oxygen. We observe that the tin AES signature can be decreased either by sputtering or by prolonged annealing above 900 K. The outward diffusion of sulfur at various temperatures above 900 K is roughly a linear function of time, on time-scales relevant to vacuum annealing and cleaning procedures useful in applied surface science studies.

Acknowledgements

Acknowledgement is made to the Donors of the American Chemical Society Petroleum Research Fund for partial support of this research. We would also like to thank Mr. Justin Tokash for spot-welding the sample, and Wah Chang for providing the Zry-4 material.

References

- [1] W. Kim, K.S. Jung, B.H. Choi, H.S. Kwon, S.J. Lee, J.G. Han, M.I. Guseva, M.V. Atamanov, *Surf. Coat. Technol.* 76–77 (1995) 595.
- [2] L. Xiaoyang, B. Xinde, Z. Chunlan, W. Long, *Surf. Coat. Technol.* 182 (2004) 138.
- [3] X.D. Bai, X.W. Chen, J. Xu, Q.G. Zhou, B.S. Chen, *Nucl. Instrum. Methods B* 217 (2004) 293.
- [4] X.D. Bai, S.G. Wang, J. Xu, J. Bao, H.M. Chen, Y.D. Fan, *J. Nucl. Mater.* 254 (1998) 266.
- [5] H.S. Hong, S.J. Kim, K.S. Lee, *J. Nucl. Mater.* 304 (2002) 8.
- [6] H.S. Hong, S.J. Kim, K.S. Lee, *J. Nucl. Mater.* 238 (1996) 211.
- [7] H.S. Hong, J.S. Moon, S.J. Kim, K.S. Lee, *J. Nucl. Mater.* 297 (2001) 113.
- [8] A. Grandjean, Y. Serruys, *J. Nucl. Mater.* 273 (1999) 111.
- [9] H.S. Hong, S.J. Kim, K.S. Lee, *J. Nucl. Mater.* 273 (1999) 177.
- [10] E.A. Garcia, G. Beranger, *J. Nucl. Mater.* 273 (1999) 221.
- [11] A.J.G. Maroto, R. Bordoni, M. Villegas, A.M. Olmedo, M.A. Blesa, A. Iglesias, P. Koenig, *J. Nucl. Mater.* 229 (1996) 79.
- [12] G.E. Fernandez, G. Meyer, H.A. Peretti, *J. Alloys Compd.* 330–332 (2002) 483.
- [13] G.E. Fernandez, G. Meyer, *J. Nucl. Mater.* 279 (2000) 167.
- [14] G. Meyer, M. Kobrinsky, J.P. Abriata, J.C. Bolcich, *J. Nucl. Mater.* 229 (1996) 48.
- [15] Y.C. Kang, R.D. Ramsier, *Surf. Sci.* 519 (2002) 229.
- [16] N. Stojilovic, Y.C. Kang, R.D. Ramsier, *Surf. Interface Anal.* 33 (2002) 945.
- [17] N. Stojilovic, R.D. Ramsier, *Solid State Commun.* 130 (2004) 623.
- [18] N. Stojilovic, D.W. Weber, R.D. Ramsier, *Appl. Surf. Sci.* 218 (2003) 188.
- [19] L.R. Danielson, *J. Vac. Sci. Technol.* 20 (1982) 86.
- [20] C. Zhang, P.R. Norton, *J. Nucl. Mater.* 300 (2002) 7.
- [21] C.-S. Zhang, B.J. Flinn, P.R. Norton, *Surf. Sci.* 264 (1992) 1.
- [22] G.B. Hoflund, G.R. Corallo, D.A. Asbury, R.E. Gilbert, *J. Vac. Sci. Technol. A* 5 (1987) 112.
- [23] Y.M. Wang, Y.S. Li, K.A.R. Mitchell, *Surf. Sci.* 342 (1995) 272.
- [24] P.C. Wong, K.A.R. Mitchell, *Can. J. Chem.* 64 (1986) 2409.
- [25] J.S. Foord, P.J. Goddard, R.M. Lambert, *Surf. Sci.* 94 (1980) 339.
- [26] Y.C. Kang, M.M. Milovancev, D.A. Clauss, M.A. Lange, R.D. Ramsier, *J. Nucl. Mater.* 281 (2000) 57.
- [27] Y.C. Kang, R.D. Ramsier, *J. Nucl. Mater.* 303 (2002) 125.
- [28] N. Stojilovic, R.D. Ramsier, *Chem. Phys. Lett.* 399 (2004) 53.
- [29] W.T. Moore, P.R. Watson, D.C. Frost, K.A.R. Mitchell, *J. Phys. C Solid State Phys.* 12 (1979) L887.
- [30] T. Tanabe, M. Tomita, *Surf. Sci.* 220 (1989) 333.
- [31] A.E. Prodromides, C. Scheuerlein, M. Taborrelli, *Appl. Surf. Sci.* 191 (2002) 300.
- [32] C.-S. Zhang, B.J. Flinn, I.V. Mitchell, P.R. Norton, *Surf. Sci.* 245 (1991) 373.
- [33] C.-S. Zhang, B. Li, P.R. Norton, *J. Nucl. Mater.* 223 (1995) 238.
- [34] K. Ojima, K. Ueda, *Appl. Surf. Sci.* 165 (2000) 141.