

Interaction of oxygen with the ordered Ni₃Al(111) alloy surface: adsorption and oxide islands formation at 800 K and 1000 K

B. -C. Kang and J. -H. Boo*

Department of Chemistry and RIAN in Institute of Basic Science, Sungkyunkwan University, Suwon 440-746

(Received August 30 2007)

The interaction of oxygen with the ordered Ni₃Al(111) alloy surface at 800 K and 1000 K has been investigated using LEED, STM, HREELS, UPS, and PAX. The clean Ni₃Al(111) surface exhibits a “2×2” LEED pattern corresponding to the ordered bulk-like terminated surface structure. For an adsorption of oxygen at 800 K, LEED shows an unrotated oxygen induced superstructure with a lattice spacing of 2.93 Å in addition to the (1×1) substrate spots. The combined HREELS and the UPS data point to an oxygen *chemisorption* on threefold aluminum sites while PAX confirms an islands growth of the overlayer. Since such sites are not available on the Ni₃Al(111) surface, we conclude the buildup of an oxygen covered aluminum overlayer. During oxygen exposure at 1000 K, however, we observe the growth of γ'-Al₂O₃ structure on the reordered Ni₃Al(111) substrate surface. This structure has been identified by means of HREELS and STM. The HREELS data will show that at 800 K the oxidation shows a very characteristic behavior that cannot be described by the formation of an Al₂O₃ overlayer. Moreover, the STM image shows a “Strawberry” structure due to the oxide islands formation at 1000 K. Conclusively, from the oxygen interaction with Ni₃Al(111) alloy surface at 800 K and 1000 K an islands growth of the aluminum oxide overlayer has been found.

Keywords : Oxygen chemisorption, Ordered Ni₃Al(111) alloy surface, LEED, STM, HREELS, UPS, and PAX.

I. Introduction

The oxidation of NiAl alloy single crystal surfaces has been studied by a number of different groups in the past year [1-6]. As a general trend the formation of a variety of well-ordered Al₂O₃ thin overlayer structures has been observed at elevated temperatures (>1000 K). In the temperature range below 1000 K the results are more complex and depend strongly on the alloy composition and crystallographic orientation of the surface. On NiAl(111), for example, a thin amorphous Al₂O₃ layer is formed at 300 K, which changes to a thin well-ordered γ'-Al₂O₃ film after annealing at 900 K[1]. In the following we will use the notation γ'-Al₂O₃ to distinguish the ultrathin alumina films from the well-known γ-Al₂O₃ bulk oxide. On NiAl(110) a disordered aluminum oxide is formed at room temperature, whereas at higher tem-

peratures a well-ordered thin film of γ'-Al₂O₃ is formed with a two domain structure [2].

Ni₃Al orders in the well-known Cu₃Au structure with a nearest neighbor distance of 2.54 Å. The (111) surface possesses a bulk-like termination with the aluminum atoms forming a 2×2 superstructure. The surface lattice parameter is 5.08 Å²[3]. The oxidation of the Ni₃Al(111) surface has already been studied by Bardi *et al.* [4] by means of XPS, LEED, and LEIS. These authors reported the growth of an oxide overlayer at temperatures above 700 K. No formation of nickel oxide species had been found, and the structure of γ'-Al₂O₃ layer grown at 900 K was claimed to possess a well-ordered (6√3×6√3)R30° periodicity, indicating an island growth. The growth mode was characterized as island growth. For the oxygen adsorptions on Ni₃Al(110) and on Ni₃Al(100) surfaces, on the other hand, islands of aluminum oxide

* [E-mail] jhboo@skku.edu

are formed at ca. 1000 K. These islands are randomly orientated with respect to the substrate surface [5,6].

Our work presented here gives to some extent complementary results (STM, HREELS, UPS, PAX) to those of Bardi *et al.* We confine ourselves to the discussion of the oxygen adsorption on Ni₃Al(111) at 800 K and 1000 K because the results obtained for these temperatures are of particular interest. In particular the HREELS data will show that at 800 K the oxidation shows a very characteristic behavior that cannot be described by the formation of an Al₂O₃ overlayer.

II. Experiment

The experiments were performed in two different ultra high vacuum (UHV) systems on the same sample. Both systems are equipped with facilities for Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and scanning tunneling microscopy (STM) and operate at base pressures of about 10⁻⁸ Pa. The photoemission spectra (PAX, UPS) were measured angle-integrated with a hemispherical analyzer at a resolution of 300 meV. A helium gas discharge lamp was used as photon source and delivered high count rates both at Helium I (21.21 eV) and Helium II (40.8 eV) energies. The energy loss spectra were measured in the second UHV system with a HREELS spectrometer (VSW IB 2000) capable of a resolution of 2 meV. In the present work the spectra have been taken at specular geometry with a resolution of about 2.5 meV at primary electron energies of about 5 eV. The Ni₃Al(111) crystal was oriented by the Laue technique with an accuracy of 0.5°. The surface was mechanically polished. Preparation in the UHV system was performed by cycles of sputtering and subsequent annealing between 1000 K and 1100 K [8]. The cleanliness of the surface was controlled with AES, LEED, STM, UPS, and HREELS, which proved to be sensitive techniques to the main contaminants oxygen and water. As a rule, two cycles of sputtering

and annealing before each experiment were sufficient to obtain a well-ordered and clean surface. In the course of the experiments it appeared, that in some cases the UPS results displayed a dependence on the oxygen pressure. Therefore, all exposures were performed at an oxygen pressure of about 2.4×10⁻⁶ Pa. Because the experiments were performed in two different UHV systems care was taken to correct the values for the oxygen exposures to the equivalent doses in both UHV systems.

III. Results and Discussion

The single crystal of Ni₃Al used in this study crystallizes in the face centered cubic (fcc) structure. Thus the hexagonal (111)-plane shows a bulk-like termination resulting in a "2×2" arrangement of the aluminum atoms in the surface layer. Figure 1 shows the LEED pattern of the clean Ni₃Al(111) surface. It is characterized by the large surface unit cell (5.08 Å) caused by the alloy order leading to a small unit cell in the reciprocal lattice. This structure has already been described by Sondericker [3] from LEED I-V measurements and is clearly visible in the STM-image (tunneling parameters: size= 6.2×7.7 nm², I_T=1.5 nA, U_B=20 mV) in figure 2. Taking into

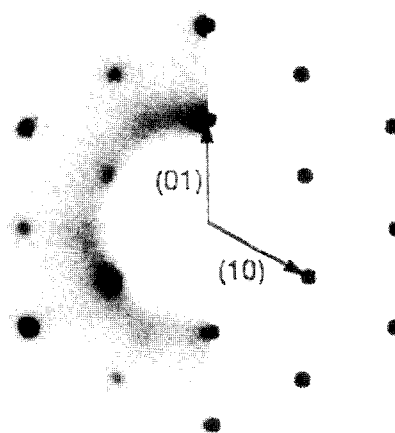


Fig. 1. LEED pattern of the clean Ni₃Al(111) surface. The right hand side shows a schematic representation.



Fig. 2. STM image of the clean $\text{Ni}_3\text{Al}(111)$ alloy surface. Tunneling parameters: size= (6.2×7.7) nm^2 , $I_t = 1.5$ nA, $U_B = 20$ mV.

account the anomalously strong atomic corrugations by aluminum atoms in STM-image [7], the superstructure is taken to represent the distribution of the Al-atoms with a lattice spacing of ca. 0.5 nm.

Comparing this "2×2" LEED structure to the LEED pattern after adsorption of 8 L oxygen at 800 K (Fig. 3), we can see that in the latter case the first order spots of the ordered alloy surface have disappeared. Thus the order of the alloy in the top most layers sensed by LEED must have disappeared. However, the new surface unit cell coincides with the second order spots of the clean alloy surface. This means that the surface unit cell has now half the lattice spacing. Additionally, oxygen induced spots formed an unrotated inner hexagon. The overlayer spots are surrounded by additional spots forming little hexagons (open circles). These additional spots can be constructed from the substrate and overlayer spots using a multiple scattering approach. The analysis of the overlayer spots leads to a lattice constant of 2.93 Å. SEXAFS measurements of Stoehr *et al.* [8] yielded a next-neighbor oxygen distance of 2.90 ± 0.05 Å for oxygen chemisorbed in threefold sites on Al(111) in excellent agreement with our results.

In order to point out an oxygen *chemisorption* on threefold aluminum sites, the combined HREELS and the ultra-violet photoemission spectra (UPS) data were

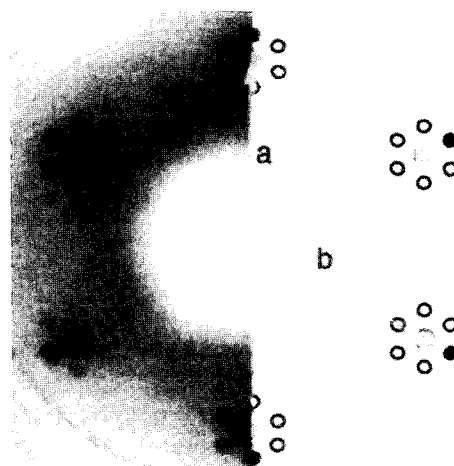


Fig. 3. LEED image of the oxygen exposed (8 L) $\text{Ni}_3\text{Al}(111)$ surface at 800 K. The right hand side image shows a schematic representation. Small black circles: substrate spots; big black circles: overlayer spots; open circles: multiple scattering spots.

used while photoemission of adsorbed xenon (PAX) confirms an islands growth of the overlayer. In figure 4a, a series of HeI-UPS spectra taken as a function of oxygen exposure at 800 K is shown. The spectra exhibit a sharp peak at a binding energy of $E_B^F = 7.0$ eV, that can be attributed to the emission from the 2p states of adsorbed oxygen atoms. The halfwidth of this peak is about 1.6 eV. For higher oxygen exposures a second peak appears at 8.8 eV. The shape of both peaks is independent of oxygen exposure. Therefore, we conclude that the *electronic state* of the oxygen remains unchanged throughout the entire coverage range. The appearance of the well resolved sharp emission at 7.0 eV is strong hint for oxygen in a single adsorption state as it is expected for chemisorption on a sp-metal like aluminum. In fact the spectra exhibit a great resemblance to the spectrum of chemisorbed oxygen on Al(111) by Eberhardt and Himpsel [9] taken with synchrotron radiation ($h\nu = 30$ eV). A slight difference in the O(2p)-peak position may arise from the fact that a different photon energy had been used since a similar shift has been observed in our experiments when using HeI radiation. These results indicate that an oxygen chemisorption on threefold aluminum sites has been

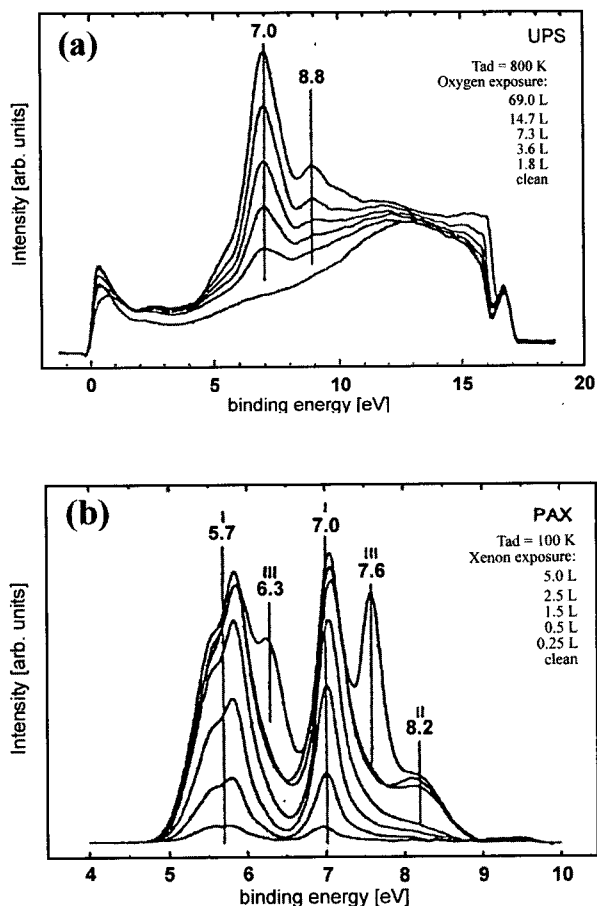


Fig. 4. Hel UP and PAX spectra of the clean and the oxygen exposed Ni₃Al(111) alloy surface: (a) Hel UPS and (b) PAX. The oxygen exposure was performed at 800 K and the PAX(Xe 5p_{3/2}, 5p_{1/2} emission) spectra was obtained from the surfaces which covered with different Xe amounts (exposures of 0 L, 0.25 L, 0.5 L, 1.5 L, 2.5 L, 5.0 L at 100 K, respectively) after 8 L oxygen exposure at 800 K. The corresponding oxygen exposures of Hel UP spectra are given in the graph.

occurred rather than oxidic species formation.

The photoemission of adsorbed xenon (PAX) was mainly used to determine the growth mode of the overlayer and the work function change during oxygen adsorption. For the PAX measurements, after 8 L oxygen exposure at 800 K, the substrate was cooled down to 100 K and Xe gas was then introduced with different Xe exposures of 0 L, 0.25 L, 0.5 L, 1.5 L, 2.5 L, 5.0 L, respectively. In figure 4b, a set of PAX spectra taken after 8 L oxygen exposure at 800 K is presented. At

first, a Xe peak group (I) with the 5p_{1/2} emission at 7.0 eV and a FWHM of 320 meV, which is attributed to Xe adsorption on bare surface sites, develops while that with 5p_{3/2} emission is appeared at 5.7 eV. Further Xe exposure leads to the development of a second peak group (II) which has a broad 5p_{1/2} emission at 8.2 eV. The corresponding 5p_{3/2} emission at 6.3 eV coincides with the 5p_{1/2} emission of the third peak group (III) at 7.6 eV, which results from Xe on Xe in the second layer, proving saturation of the first Xe layer. The coexistence of the two peak groups (I) and (II) in the first Xe layer can only be explained by the presence of two different adsorption sites for the Xe atoms, which we attribute to Xe adsorption on bare surface sites (I) and Xe adsorption on oxygen covered islands (II). The peak group (I) has also been detected for the adsorbed xenon on the clean Ni₃Al(111) surface.

According to the PAX model [10] the local work function Φ_{loc} of this overlayer is given by

$$\Phi_{loc} = E_B^{vac} - E_B^F$$

where $E_B^{vac} = 12.3 \pm 0.1$ eV is the 5p_{1/2} electron binding energy with respect to the vacuum level and E_B^F is the 5p_{1/2} electron binding energy (8.2 eV for the Xe adsorption on oxygen covered islands) with respect to the Fermi level, in each case for the adsorbed xenon. Thus, the work function of overlayer islands can be estimated to be 4.1 eV. Gartland [11], who performed photoelectrical work function measurements of oxygen on Al(111), found a work function increase of about 100 meV to a final value of 4.35 eV for the chemisorbed phase. This coincides with photoelectrical measurements of Eberhardt and Himpsel [9] who also estimated the work function increase for chemisorbed oxygen on Al(111) to be 100 meV. Considering the uncertainty of absolute work function determinations as well as the different experimental conditions (i. e. local work function from PAX versus average work function) it can be stated that the work function found for oxygen adsorption at 800 K on Ni₃Al(111) reasonably fits the values estimated for chemisorbed oxygen on Al(111).

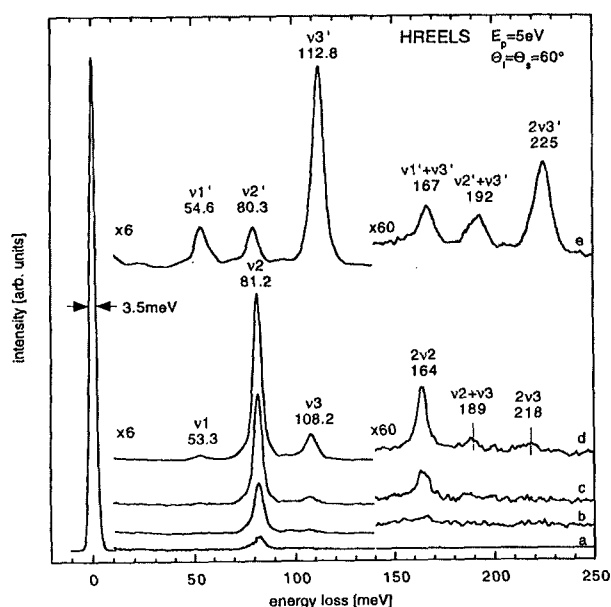


Fig. 5. HREEL spectra obtained after different oxygen exposures. For oxygen adsorption at 800 K, the corresponding exposures are: a) 4 L, b) 8 L, c) 20 L, and d) 40 L. Spectrum e) shows the result after annealing the 40 L exposure to 1000 K.

Like the UPS measurements this suggests the existence of oxygen chemisorbed on aluminum sites.

In order to clarify the nature of the oxygen bonding to the surface HREELS experiments have been undertaken. Figure 5 shows a series of HREEL spectra for increasing oxygen exposure at 800 K. A very intense feature appears at a loss energy of 81.2 meV (v_2). Two further peaks are found at 108.2 meV (v_3) and 53.3 meV (v_1). These features coincide with the results by Strong *et al.* for Al_2O_3 on $\text{Al}(111)$ with losses at about 50 meV, 80 meV, and 105 meV [12]. Strong *et al.* attributed the loss feature at 80 meV to a stretch mode of chemisorbed oxygen vibrating perpendicular to the surface with the oxygen being adsorbed on the fcc sites of the $\text{Al}(111)$ surface. The feature at 105 meV arises from subsurface oxygen adsorbed in tetrahedral sites, whereas the loss peak at about 50 meV is a result of the coupling of two aluminium layers through subsurface oxygen [13]. If we adopt this assignment we can conclude from the high intensity of the loss v_2 , that the oxygen is chemisorbed on the $\text{Ni}_3\text{Al}(111)$ surface on threefold aluminum hollow

sites. The losses at 108.2 meV and 53.3 meV point out some amounts of subsurface oxygen. The three peaks at higher loss energies are multiple losses. It can also be seen from figure 5 that the peak positions of the three losses v_1 , v_2 , v_3 are constant for all oxygen exposures. Accordingly, the binding geometry of the chemisorbed oxygen (and of the oxidic oxygen) does not change with coverage, which points to an island growth mechanism of the overlayer. Since such threefold hollow sites are not available on the $\text{Ni}_3\text{Al}(111)$ surface, however, we conclude the buildup of an oxygen covered aluminum overlayer. Moreover, for comparison the HREEL spectrum of a surface that had been annealed to 1000 K is shown in figure 5 (curve e). Here the peak positions and intensities are identical to the positions and intensities found by Jaeger *et al.* [2] for $\gamma\text{-Al}_2\text{O}_3$ on $\text{NiAl}(110)$. Franchy *et al.* [1] also found a very similar HREEL spectra for $\gamma\text{-Al}_2\text{O}_3$ formation on $\text{NiAl}(111)$ with losses at 53, 79, and 110 meV. Thus, it can be concluded that $\gamma\text{-Al}_2\text{O}_3$ is formed after annealed the chemisorbed oxygen on $\text{Ni}_3\text{Al}(111)$ at 1000 K and the HREEL spectra for oxygen adsorption at 800 K point to the existence of oxygen chemisorbed on the aluminum sites. With STM the formation of aluminum oxide islands was clearly confirmed.

Previous LEED and HREELS measurements already suggested the formation of a rough oxidic layer on $\text{Ni}_3\text{Al}(111)$ for oxygen exposure at 300 K [14]. If the highly disordered oxide structure grown at 300 K is annealed at 1000 K for 2 min nicely ordered oxide islands on the $\text{Ni}_3\text{Al}(111)$ terraces can be produced. A "strawberry" structure can be taken under the tunneling parameters of size=(144×144) nm², $I_T=1.0$ nA, $U_B=2000$ mV, as we would like to call them for apparent reasons, are shown in figure 6. Closer inspection of the STM images shows that the array of bright spots is well-ordered. Additionally, two rotational domains can be identified. Applying pair correlation methods, the radial distribution of the bright spots on the islands and the rotational distribution of the islands can be deduced.

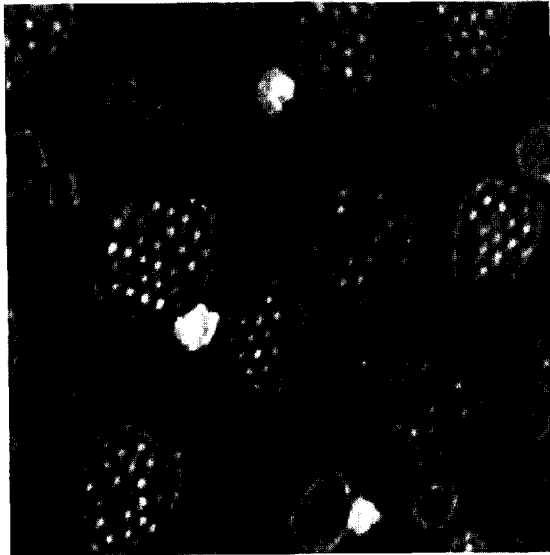


Fig. 6. STM image for the "strawberry" structure of the oxide islands grown at 1000 K on Ni₃Al(111) alloy surface. Tunneling parameters: size=(144x144) nm², I_T=1.0 nA, U_B=2000 mV.

It turns out that the mean distance between the spots on the islands is 4.6 nm and the two rotational domains have an angle of 24.6°. This is in line with the results of Bardi *et al.* who estimated the thickness of the oxide film from XPS to be 5 Å [4], indicating that the film consists of two O/Al bilayers. Unfortunately, however, it is not possible to explain the origin of the bright spots from this STM image alone. Moreover, they should be a Moiré structure that is supported by the results for the oxide directly grown at 1000 K where a similar superstructure can be identified as Moiré pattern.

IV. Conclusions

From the experimental results presented in this work a number of conclusions concerning the oxygen adsorptions on Ni₃Al(111) at 800 K and 1000 K can be drawn. First of all an island growth of the overlayer has been found. This result is in line with all previous investigations of this and similar NiAl alloy surfaces at similar temperatures [1-3]. However, the UPS and HREELS results show clearly that in the present case a *chemisorbed* oxygen layer is favored over the

formation of an Al₂O₃ overlayer. Since no evidence for a nickel-oxygen interaction has been found the oxygen must be chemisorbed on aluminum. The formation of the aluminum layer can be explained by aluminum segregation to the topmost layer. This aluminum segregation explains the disappearance of the alloy order detected in LEED as it also results in an aluminum depletion in deeper alloy layers. The segregation of the aluminum to the topmost layer can be described as an adsorbate (oxygen) induced segregation as it has already been observed by Shen *et al.* for the (001) and (011) surfaces of Ni₃Al [4]. All features found in HREELS and UPS can then be explained by chemisorption of oxygen on this aluminum layer in good agreement with the results obtained for chemisorbed oxygen on bulk Al(111) [7,8]. The structure of the overlayer is characterized by a large coincidence mesh where 13 overlayer atoms are placed on 15 substrate atoms. The overlayer is constituted by an aluminum layer covered with chemisorbed oxygen, the oxygen being most likely adsorbed in threefold hollow sites.

Acknowledgements

We thank to professor Klaus Wandelt in the Bonn University, Germany, for his profitable discussions and comments. This work was supported by the Korea Research Foundation Grant funded by the Korean Government(MOEHRD, Basic Research Promotion Fund) (KRF-2005-005-J11902).

References

- [1] R. Franchy, J. Masuch, and P. Gassmann, *Appl. Surf. Sci.* **93**, 317 (1996).
- [2] R. M. Jaeger, H. Kuhlenbeck, H. -J. Freund, M. Wuttig, W. Hoffmann, R. Franchy, and H. Ibach, *Surf. Sci.* **259**, 235 (1991).
- [3] D. Sondicker, F. Jona, and P. M. Marcus, *Phys. Rev.* **B34**, 6770 (1986).

- [4] U. Bardi, A. Atrei, and G. Roviida, *Surf. Sci.* **286**, 87 (1992).
- [5] Y. Shen, D. J. O'Connor, and R. J. MacDonald, *Nucl. Instr. & Meth.* **B67**, 350 (1992).
- [6] Y. Shen, D. J. O'Connor, and R. J. MacDonald, *Surf. Interface Anal.* **17**, 903 (1991).
- [7] J. Wintterlin, J. Wiechers, H. Brune, T. Gritsch, H. Hofer, and R. J. Behm, *Phys. Rev. Lett.* **62**, 59 (1989).
- [8] J. Stoehr, L. I. Johansson, S. Brennan, M. Hecht, and J. N. Miller, *Phys. Rev.* **B22**, 4052 (1980).
- [9] W. Eberhardt and F. J. Himpsel, *Phys. Rev. Lett.* **42**, 1375 (1979).
- [10] K. Wandelt, *J. Vac. Sci. Technol.* **A2**, 802 (1984).
- [11] P. O. Gartland, *Surf. Sci.* **62**, 183 (1977).
- [12] R. L. Strong and J. L. Erskine, *J. Vac. Sci. Technol.* **A3**, 1428 (1985).
- [13] R. L. Strong, B. Firey, F. W. deWette, and J. L. Erskine, *Phys. Rev.* **B26**, 3482 (1982).
- [14] C. Becker, J. Kandler, H. Raaf, R. Linke, T. Pelster, M. Draeger, M. Tanemura, and K. Wandelt, *J. Vac. Sci. Technol.* **A16**, 1000 (1998).

Ordered Ni₃Al(111) 합금표면과 산소와의 상호작용 : 800 K와 1000 K에서의 흡착과 oxide islands 형성연구

강병창 · 부진호*

성균관대학교 화학과 및 기초과학연구소, 수원 440-746

(2007년 8월 30일 받음)

800 K와 1000 K에서 ordered Ni₃Al(111) 합금표면과 산소기체와의 상호작용을 LEED, STM, HREELS, UPS, 그리고 PAX를 이용 고찰하였다. 산소가 없는 깨끗한 Ni₃Al(111) 표면에 대한 LEED 측정결과 어떤 “2×2” 패턴이 관측되었는데, 이는 규칙적인 벌크와 같은 terminated 표면구조를 가짐을 의미한다. 그러나 800 K로 유지된 같은 표면에 산소를 흡착시킨 후 LEED를 관찰하면 (1×1) substrate spots 외에 산소에 의해 유발된 lattice spacing이 2.93 Å 인 어떤 회전되지 않은 superstructure가 얻어졌다. 이를 자세히 규명하기 위해 HREELS와 UPS를 측정한 결과 threefold aluminum 자리에 산소들이 화학흡착됨을 알 수 있었고, 아울러 PAX 측정결과 흡착된 overlayer들이 어떤 oxide island 형태로 성장됨을 보여주었다. 그러나 실질적으로 Ni₃Al(111) 표면에서는 그러한 자리들이 유효하지 않기 때문에 우리들은 oxide island 생성은 Ni₃Al(111) 표면에 있는 aluminum overlayer들을 덮음으로써 성장되고 있다고 결론을 내렸다. 한편, 1000 K로 유지된 Ni₃Al(111) 표면에 산소를 노출하면 γ -Al₂O₃ 구조가 성장됨을 HREELS와 STM 측정결과로부터 알 수 있었다. 그리고 HREELS 측정결과, 800 K에서 산화는 매우 특이한 양상을 띠며 일어나고 있으나 정확하게 Al₂O₃ overlayer가 형성되는 경우와는 일치하지 않음을 알 수 있었고, 1000 K에서 산소노출 후 얻은 STM 영상 역시 oxide island 들이 형성에 기인된 어떤 “Strawberry” 구조를 보여주었으나 정확하게 Al₂O₃ overlayer가 형성되었는지는 규명할 수 없었다. 결론적으로, 800 K와 1000 K에서 Ni₃Al(111) 합금표면위의 산소 상호작용결과 어떤 aluminum oxide overlayer의 island들이 성장됨을 확인할 수 있었다.

주제어 : 산소화학흡착, Ordered Ni₃Al(111) 합금표면, 저에너지전자회절(LEED), 주사형터널현미경(STM), 고분해능전자에너지손실분광기(HREELS), 자외선광전자분광기(UPS), 제논흡착광전자분광기(PAX).

* [전자우편] jhboo@skku.edu