O₂ dissociation in Na-modified gold ultrathin layer on Cu(111)

Antonio Politano^{a,*} and Gennaro Chiarello^{a,b}

www.goldbulletin.org

Abstract

High-resolution electron energy loss spectroscopy has been used to investigate the catalytic properties of Na-doped Au monolayer grown on Cu(111). The presence of Na atoms allows the dissociation of oxygen molecules and the stabilization of atomic oxygen. The strong reduction of the dissociation barrier for O_2 promoted by Na could readily favor many surface chemical reactions, due to the key role of atomic oxygen in many oxidation processes catalyzed by gold.

Present address: Departamento de Fisica de la Materia Condensada, Universidad Autonoma de Madrid, 28049, Madrid, Spain

- ^a Dipartimento di Fisica, Università degli Studi della Calabria, 87036 Rende(Cs), Italy
- ^b CNISM, Consorzio Nazionale Interuniversitario per le Scienze Fisiche della Materia
- * Corresponding author E-mail: antonio.politano@fis.unical.it

Keywords: electron energy loss spectroscopy (EELS), gold films, alkali atoms, oxygen, dissociation

Introduction

In recent years chemical reactions at bimetallic surfaces are attracting a great attention [1-13] for both fundamental interest and technological applications. Metal/metal interfaces show novel physical and chemical properties [4, 9, 14-16]. In particular, bimetallic surfaces involving gold [7, 17-19] are extensively investigated due to the high catalytic activity of nanostructured gold systems [20-23].

Atomic oxygen has been demonstrated to play an important role in promoting a quantity of selective oxidation processes on gold systems [24]. Hence, several papers have been devoted to understanding the role of oxygen-induced reactivity of Au-based catalysts [25-49] as it is mandatory to shed light on the nature of the various preliminary and/or intermediate Au-O complexes involved in these reactions. It has been demonstrated that oxygenprecovered gold flat surfaces are reactive toward water, [32] carbon monoxide [38] carbon dioxide [50, 51], acetylene [52], ammonia [39], amines [53], methanol [52], and alcohols [54-56]. Limitations in the partial oxidation reactions catalyzed on gold surfaces [22, 23, 42, 43, 53, 57-66] are related to the low O₂ dissociation rate [42]. The dissociation probability for O₂ on single-crystal Au surfaces has been found to be extremely small [<<10⁻⁶ as reported] in Ref. 47]. To overcome the high dissociation barrier [67, 68] for O₂, different methods have been used for stabilizing oxygen atoms on gold (atomic O sources [69], thermal dissociation [70], oxygen-ion sputtering [71], microwave discharge [72], electron bombardment of physisorbed layers of oxygen [73, 74] and the usage of reactive molecules such as NO₂[60] or O₂ [57, 59, 75, 76]).

However, it is also well known that Au can be activated as a catalyst [20, 46, 77-81] by depositing

small particles in the range of 2 to 5 nm on suitable oxide supports, such as titania [44, 45, 58, 82] and ceria [83-85]. A size effect on the efficiency of Au nanoparticles-based catalysts exists. Larger deposited Au particles show lower catalytic activity. This could be closely associated with the charge density of the surface Au atoms. The surface negative charge decreases with the size of the Au clusters. Anionic Au atoms in the cluster have a stronger interaction with O_2 than a neutral Au atom [20, 63, 86-95]. These findings suggest that the active sites for oxygenation on the supported and unsupported Au catalysts [63, 93, 96] are Au atoms which are negatively charged.

Gold thin films deposited on Cu(111) offer the opportunity to study the chemical activity of an unreconstructed metal/metal interface. In fact, due to the negligible lattice mismatch gold grows on Cu(111) along the [111] direction without surface reconstructions [97]. On other Cu singlecrystal surfaces the exchange diffusion mechanism of Au adatoms is activated, while it is absent on the (111) surface [98]. The gold monolayer is characterized by three-dimensional islands [99]. Room temperature deposition of Au onto Cu(111) gave a film with twinned fcc structure, a reasonable degree of crystallinity and clear indications of inter-diffusion at the interface [100]. Moreover, at room temperature, no AuCu alloy was formed [9, 12, 100, 101].

On the other hand, alkali-metal doping is a powerful tool to manipulate the physical and chemical properties of surfaces and it is widely used for tailoring new catalysts [102-109]. For these reasons, the study of alkali promotional effects on surfaces and interfaces continues to be one of the main topics of surface science [110-121].

Alkali-metal atoms form strong bonds whenever coadsorbed with Au clusters, with the formation of alkali aurides [122-130], which are particularly interesting for plasmonics [122]. The intermetallic bond in the alkali auride series is in general highly polar, with a large charge transfer from the alkali metals to gold.

However, in the Na_xAu clusters the Na-Na interaction is rather strong while the Na-Au bond is characterized by delocalized electrons exhibiting a polarized charge distribution with a slight negative charge on Au atoms [131]. Herein we report on high-resolution electron energy loss spectroscopy (HREELS) measurements on Na coadsorbed with Au on Cu(111). We found that both Au/Cu(111) and the same bimetallic surface modified by Na adsorption scarcely react with CO. On the other hand, in the Na+Au/Cu(111) a dissociative adsorption for O_2 occurs. The dissociation of oxygen molecules and the stabilization of atomic oxygen on the surface are unusual for Au and it could promote many chemical reactions at the Au/Cu(111) interface.

Experimental

Measurements were carried out in a UHV chamber operating at a base pressure of 5.10⁻⁹ Pa described elsewhere [132-134]. The sample was a single crystal of Cu(111). The surface was cleaned by repeated cycles of ion sputtering and annealing at 700-800 K. Surface cleanliness and order were checked using Auger electron spectroscopy (AES) and lowenergy electron diffraction (LEED) measurements, respectively. Gold was deposited onto the Cu(111) surface by evaporating from an Au wire wrapped on a tungsten filament. Au films were grown at very low deposition rates (≈0.03 ML/min). The occurrence of the p(1x1)-Au LEED pattern was used as the calibration point of θ_{Au} =1.0 ML (the unit of measure of coverage is the monolayer, ML, defined as the ratio between the number of atoms of the overlayer and that of the outermost layer of the surface).

The existence of Au islands is confirmed by electron reflectivity measurements.

Sodium was deposited onto the substrate by evaporating from a well-outgassed commercial getter source. The occurrence of the (3/2x3/2)-Na LEED pattern was used as the calibration point of θ_{Na} =0.44 ML. Similar results were obtained by a calibration procedure using AES. A constant sticking coefficient was assumed to obtain other desired Au and Na coverage. A particular care has been devoted to avoid contamination of alkalis [16, 114, 132, 135].

Oxygen and carbon monoxide exposures were carried out by using precision leak valves.

HREEL experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS). The incident angle with respect to the sample normal was fixed at 55.0°. The acceptance angle of our spectrometer is $\pm 0.5^{\circ}$. The primary energy was set to 3 eV in all measurements. The energy resolution of the spectrometer was degraded to 5 meV so as to increase the signal-to-noise ratio of loss peaks.

All depositions and measurements were made at room temperature, at which no trace of AuCu alloy was revealed in both LEED and AES measurements.

Results

In order to put in evidence the effects of the adsorption of a gold monolayer on the catalytic properties, firstly we have investigated the coadsorption of Na with CO and oxygen in the absence of gold. Results are reported in figure 1.

Carbon monoxide was dosed (1 L, 1 L= $1.33 \ 10^{-6}$ mbar·s) at room temperature on 0.20 ML of Na deposited at the same temperature on Cu(111).



HREEL spectra for the clean Cu(111) substrate and for 0.20 ML Na/Cu(111) exposed at 300 K to CO and successively to O_2 . All spectra were multiplied by the same factor. (inset): HREEL spectra of 0.06 ML Na/Cu(111) exposed to 6 L O_2 at room temperature. The presence of subsurface O is argued from the appearance of the 58 meV peak [119, 136]

The shoulder at 21 meV in the HREEL spectrum of the Cu(111) in principle could be assigned to the excitation of the S_3 acoustic resonance [137, 138], which has however a large amplitude at the zone boundary and is localized on the second layer. Thus this mode should not be observed in the scattering regime of these experiments. We assign this feature to the broad zone-center optical phonon [139, 140]

Beside the Na-Cu vibration [141-143], which shifted from 19 down to 17 meV upon CO adsorption due to the CO-induced lengthening of the alkali-substrate bond [144-147], also the Na-O vibration at 36 meV has been revealed [114, 148]. This is ascribed to the dissociative adsorption of CO on alkali-promoted Cu(111) which we have recently demonstrated elsewhere [149]. The intensity of the Na-O feature increased upon oxygen adsorption. On the other hand, the progressive decrease of the intensity of the Na-Cu stretch is ascribed to the formation of the bond between Na and O.

In figure 2 we report HREELS measurements for a common exposure of 1 L of CO on Cu(111) (spectrum a) and 1 ML Au/Cu(111) (spectrum b). At room temperature, CO does not adsorb on Cu(111) and on a single Au layer deposited on Cu(111), as indicated by the absence of CO-related vibrations in HREEL spectra.

In order to verify the effects of the adsorption of submonolayers of alkalis on the chemical reactivity of the Au/Cu(111) bimetallic surface, 0.20 ML of Na deposited on a single layer of Au on Cu(111) were exposed to 1 L of CO (Figure 2, spectrum c). No CO adsorption occurs, in contrast with the dissociative adsorption revealed in the absence of gold (Figure 1). Upon oxygen exposure (6 L at room temperature, spectrum d), two loss features appeared. A double-exponential background was subtracted from spectrum (d) and the resulting spectrum was fitted with two Gaussian line-shapes. Fit procedure revealed the existence of loss peaks at 35 and 43 meV (inset of Figure 2). They were assigned to the Na-O [120, 146, 150] vibration and the O-Au [151] stretching, respectively.

The analysis of the frequency of the O-Au vibration indicates the occurrence a three-fold coordination of O with respect to Au atoms [151].

It is worth noticing that in the absence of gold oxygen adatoms could adsorb in over-surface adsorption sites only in the close vicinity of alkalis, as indicated



HREEL spectra for a common CO exposure of 1 L at room temperature on: (a) the clean Cu(111) substrate; (b) 1 ML of Au on Cu(111); (c) 0.20 ML Na/Au/Cu(111). Spectrum (d) reports the HREEL spectrum for the sample of the spectrum (c) exposed to 6 L of O_2 at room temperature. The inset shows the fit with two Gaussian line-shapes centered at 35 and 43 meV of the spectrum (d) after the subtraction of a double-exponential background

by the absence of the O-Cu vibration at 46 meV [119, 152]. In particular, for sufficiently high coverages of Na, the Na-O stretch appeared at 36 meV (Figure 1), while for low Na coverages (Na doping) the oxygen adatoms are allocated in subsurface sites of Cu(111) [119] (inset of the same figure), as indicated by the occurrence of the vibrational peak at 58 meV.

It is worth mentioning that for O/Ag(100) also localised *d*-*d* transitions can be observed during the initial stages of surface oxidation [153].

The absence of the Na stretching mode indicates a reduced ionic character of surface chemical bonds involving alkali adatoms. In fact, it is quite expected that ionic species have a higher intensity in HREEL spectra [120, 154]. This is due to the agglomeration of Na atoms and the formation of Na_xAu_y clusters [122, 123] with a strong Na-Na interaction [131].

Hence, the weight of stretching modes is vanishing. This could be taken as a fingerprint of a reduced ionic character of the Na-substrate bond when Na is coadsorbed with Au.

It is experimentally proven that oxygen does not readily chemisorb on gold single crystals [155] or titania-supported gold clusters larger than 1 nm [156] either dissociatively or molecularly.

Density functional theory (DFT) calculations suggest that the barrier to dissociative chemisorption of oxygen on gold is very high and also that molecularly chemisorbed oxygen is not stable on clean Au(111) [34, 67, 157].

The lowest barrier is 0.93 eV, which occurs on steps [34]. It is expected that O_2 cannot dissociate at low temperatures, but it may be possible on steps at elevated temperatures. Instead, we observed atomic oxygen on the Na-doped Au/Cu(111) even at room temperature. This means that the dissociation barrier for O_2 on gold is significantly decreased by Na adsorption.

We ascribe the enhanced dissociation probability for oxygen molecules even at room temperature to the joint presence of Na and gold on the surface. The Na-derived slight negative charge of Au atoms in the NaAu complex [131] is expected to play a key role in such a process.

The nature of chemisorbed atomic oxygen on gold is important in elucidating the unique chemistry that has been observed over supported gold catalysts [22, 47, 48, 61, 62, 64, 158-163]. Hence, our finding deserves a particular relevance and claims for further experimental and theoretical work.

Conclusions

We have shown that atomic oxygen is stabilized in oversurface sites in the Na-doped Au/Cu(111) bimetallic system through O_2 dissociation. The adsorption of atomic oxygen in over-surface sites at room temperature could be used for obtaining a negative doping of the Au/Cu(111) bimetallic surface and for tuning its charge-density profile so as to change its chemical, physical and catalytical properties. On the other hand, the Na+Au/Cu(111) surface does not react toward CO at room temperature, in contrast to Na/Cu(111).

About the authors



Antonio Politano has obtained the PhD in Physics at the University of Calabria (Italy) in December 2008.



Gennaro Chiarello (Associate Professor) is a member of the staff of the SPES group (Electronic Spectroscopies of Surfaces) of the Physics Department of the University of Calabria. Their investigation includes the electronic properties of ultrathin alkali and noble-metal films, the chemical reactivity of bimetallic surfaces and alkali coadsorption systems.

References

- 1 O.R. Inderwildi, S.J. Jenkins, D.A. King, *Surf. Sci.*, 2007, **601**, L103
- 2 M. Ruff, N. Takehiro, P. Liu, J.K. Norskov, R.J. Behm, Chemphyschem, 2007, 8, 2068
- 3 J.R. Kitchin, J.K. Norskov, M.A. Barteau, J.G. Chen, *Phys. Rev. Lett.*, 2004, **93**, 156801
- 4 C.J. Baddeley, L.H. Bloxham, S.C. Laroze, R. Raval, T.C.
 Q. Noakes, P. Bailey, *J. Phys. Chem. B*, 2001, **105**, 2766
- 5 J.G. Chen, C.A. Menning, M.B. Zellner, *Surf. Sci. Rep.*, 2008, **63**, 201
- H. Ren, M.P. Humbert, C.A. Menning, J.G. Chen, Y. Shu,
 U.G. Singh, W.C. Cheng, *Appl. Catal. A*, 2010, **375**, 303
- 7 S. Venkatachalam, T. Jacob, *Phys. Chem. Chem. Phys.*, 2009, **11**, 3263
- A. Politano, V. Formoso, E. Colavita, G. Chiarello, *Phys. Rev. B*, 2009, **79**, 045426
- A. Politano, V. Formoso, G. Chiarello, *Appl. Surf. Sci.*, 2009, 255, 6038
- A. Politano, V. Formoso, G. Chiarello, J. El. Spec. Rel. Phen., 2009, **173**, 12
- 11 A. Politano, V. Formoso, G. Chiarello, *Superlattices Microstruct.*, 2009, **46**, 137
- A. Politano, V. Formoso, G. Chiarello, *Plasmonics*, 2008, 3, 165
- A. Politano, G. Chiarello, *Phys. Status Solidi- Rapid Res.* Lett. (RRL), 2009, 3, 136
- 14 Y. Xu, A.V. Ruban, M. Mavrikakis, J. Am. Chem. Soc., 2004, 126, 4717

- A. Politano, V. Formoso, G. Chiarello, Surf. Sci., 2009, 603, 933
- A. Politano, R.G. Agostino, E. Colavita, V. Formoso,
 G. Chiarello, *J. Chem. Phys.*, 2007, **126**, 244712
- 17 A. Piednoir, M.A. Languille, L. Piccolo, A. Valcarcel, F.J.C.S. Aires, J.C. Bertolini, *Catal. Lett.*, 2007, **114**, 110
- L.Y. Gan, Y.X. Zhang, Y.J. Zhao, *J. Phys. Chem. C*, 2010, 114, 996
- M.O. Pedersen, S. Helveg, A. Ruban, I. Stensgaard,
 E. Lægsgaard, J.K. Nørskov, F. Besenbacher, *Surf. Sci.*, 1999, **426**, 395
- 20 F. Vindigni, M. Manzoli, A. Chiorino, F. Boccuzzi, *Gold Bull.*, 2009, **42**, 106
- R.A. Ojifinni, N.S. Froemming, J. Gong, M. Pan, T.S. Kim, J.M. White, G. Henkelman, C.B. Mullins, *J. Am. Chem. Soc.*, 2008, **130**, 6801
- 22 A. Grirrane, A. Corma, H. García, Science, 2008, 322, 1661
- H. Falsig, B. Hvolbæk, I.S. Kristensen, T. Jiang, T. Bligaard,
 C.H. Christensen, J.K. Nørskov, *Angew. Chem.*, 2008, 47, 4835
- 24 R.A. Ojifinni, J. Gong, D.W. Flaherty, T.S. Kim, C.B. Mullins, *J. Phys. Chem. C*, 2009, **113**, 9820
- 25 T.S. Kim, J. Gong, R.A. Ojifinni, J.M. White, C.B. Mullins, *J. Am. Chem. Soc.*, 2006, **128**, 6282
- 26 G.C. Bond, D.T. Thompson, *Catal. Rev. Sci. Eng.*, 1999, **41**, 319
- 27 M. Haruta, T. Kobayashi, H. Sano, N. Yamada, *Chem. Lett.*, 1987, **16**, 405
- 28 J.D. Grunwaldt, A. Baiker, J. Phys. Chem. B, 1999, 103, 1002
- J.D. Stiehl, J.L. Gong, R.A. Ojifinni, T.S. Kim, S.M. McClure,
 C.B. Mullins, *J. Phys. Chem. B*, 2006, **110**, 20337
- 30 J.D. Stiehl, T.S. Kim, S.M. McClure, C.B. Mullins, J. Am. Chem. Soc., 2004, **126**, 13574
- B.K. Min, A.R. Alemozafar, D. Pinnaduwage, X. Deng,
 C.M. Friend, *J. Phys. Chem. B*, 2006, **110**, 19833
- 32 R.A. Ojifinni, N.S. Froemming, J. Gong, M. Pan, T.S. Kim, J.M. White, G. Henkelman, C.B. Mullins, *J. Am. Chem. Soc.*, 2008, **130**, 6801
- H.G. Boyen, G. Kastle, F. Weigl, B. Koslowski, C. Dietrich, P. Ziemann, J.P. Spatz, S. Riethmuller, C. Hartmann, M. Moller, G. Schmid, M.G. Garnier, P. Oelhafen, *Science*, 2002, **297**, 1533
- 34 Z.P. Liu, P. Hu, A. Alavi, J. Am. Chem. Soc., 2002, **124**, 14770
- 35 Z.P. Liu, S.J. Jenkins, D.A. King, *Phys. Rev. Lett.*, 2005, 94, 196102
- N. Lopez, J.K. Norskov, J. Am. Chem. Soc., 2002, 124, 11262
- J.L. Gong, D.W. Flaherty, R.A. Ojifinni, J.M. White,
 C.B. Mullins, J. *Phys Chem. C*, 2008, **112**, 5501
- 38 J.L. Gong, R.A. Ojifinni, T.S. Kim, J.D. Stiehl, S.M. McClure, J.M. White, C.B. Mullins, *Top. Catal.*, 2007, **44**, 57
- 39 J.L. Gong, R.A. Ojifinni, T.S. Kim, J.M. White, C.B. Mullins, J. Am. Chem. Soc., 2006, **128**, 9012

- 40 R.G. Quiller, T.A. Baker, X. Deng, M.E. Colling, B.K. Min, C.M. Friend, *J. Chem. Phys.*, 2008, **129**, 064702
- 41 K.A. Davis, D.W. Goodman, *J. Phys. Chem. B*, 2000, **104**, 8557
- 42 A. Wittstock, V. Zielasek, J. Biener, C.M. Friend, M. Baumer, Science, 2010, **327**, 319
- K. Wong, Q. Zeng, A. Yu, Chem. Eng. J. (Lausanne), 2009, 155, 824
- Y. Liu, T. Xing, Z. Wei, X. Li, W. Yan, *Catal. Commun.*, 2009, 10, 2023
- 45 K. Arve, A.J. Adam, A.O. Simakova, A.L. Čapek, K. Eränen, D.Y. Murzin, *Topics in Catalysis*, 2009, **52**, 1762
- 46 A. Hugon, L. Delannoy, C. Louis, Gold Bull., 2008, 41, 127
- 47 A. Corma, P. Serna, Science, 2006, 313, 332
- M.D. Hughes, Y.J. Xu, P. Jenkins, P. McMorn, P. Landon,
 D.I. Enache, A.F. Carley, G.A. Attard, G.J. Hutchings, F. King,
 E.H. Stitt, P. Johnston, K. Griffin, C.J. Kiely, *Nature*, 2005,
 437, 1132
- 49 A. Sanchez, S. Abbet, U. Heiz, W.D. Schneider,
 H. Häkkinen, R.N. Barnett, U. Landman, *J. Phys. Chem. A*, 1999, **103**, 9573
- R.A. Ojifinni, J.L. Gong, N.S. Froemming, D.W. Flaherty, M. Pan, G. Henkelman, C.B. Mullins, *J. Am. Chem. Soc.*, 2008, **130**, 11250
- 51 J.L. Gong, C.B. Mullins, J. Phys. Chem. C, 2008, 112, 17631
- 52 D.A. Outka, R.J. Madix, J. Am. Chem. Soc., 1987, 109, 1708
- 53 J. Gong, T. Yan, C.B. Mullins, *Chem. Comm.*, 2009, 761
- 54 R.J. Madix, C.M. Friend, X.Y. Liu, J. Catal., 2008, 258, 410
- 55 B. Xu, X. Liu, J. Haubrich, R.J. Madix, C.M. Friend, *Angew. Chem., Int. Ed.*, 2009, **48**, 1
- 56 J.L. Gong, D.W. Flaherty, T. Yan, C.B. Mullins, *Chemphyschem*, 2008, **9**, 2461
- 57 B. Xu, X. Liu, J. Haubrich, R.J. Madix, C.M. Friend, *Angew. Chem.*, 2009, **48**, 4206
- 58 T.A. Nijhuis, E. Sacaliuc-Parvulescu, N.S. Govender, J.C. Schouten, B.M. Weckhuysen, J. Catal., 2009, 265, 161
- 59 X. Liu, B. Xu, J. Haubrich, R.J. Madix, C.M. Friend, *J. Am. Chem. Soc.*, 2009, **131**, 5757
- 60 M. Turner, O.P.H. Vaughan, R.M. Lambert, *Chem. Comm.*, 2008, 2316
- M. Turner, V.B. Golovko, O.P.H. Vaughan, P. Abdulkin,
 A. Berenguer-Murcia, M.S. Tikhov, B.F.G. Johnson,
 R.M. Lambert, *Nature*, 2008, **454**, 981
- A.A. Herzing, C.J. Kiely, A.F. Carley, P. Landon,
 G.J. Hutchings, *Science*, 2008, **321**, 1331
- 63 P. Fristrup, L. Bahn Johansen, C.H. Christensen, *Chem. Comm.*, 2008, 2750
- J. Zhang, K. Sasaki, E. Sutter, R.R. Adzic, *Science*, 2007, 315, 220
- 65 B.K. Min, C.M. Friend, Chem. Rev., 2007, 107, 2709
- B. Yoon, H. Häkkinen, U. Landman, A.S. Wörz, J.M. Antonietti, S. Abbet, K. Judai, U. Heiz, *Science*, 2005, 307, 403
- 67 Y. Xu, M. Mavrikakis, J. Phys. Chem. B, 2003, 107, 9298

- 68 M. Landmann, E. Rauls, W.G. Schmidt, *Phys. Rev. B*, 2009, 79, 045412
- 69 T. Yan, J. Gong, C.B. Mullins, J. Am. Chem. Soc., 2009, 131, 16189
- A.G. Sault, R.J. Madix, C.T. Campbell, Surf. Sci., 1986, 169, 347
- J.M. Gottfried, N. Elghobashi, S.L.M. Schroeder,K. Christmann, *Surf. Sci.*, 2003, **523**, 89
- 72 C. Linsmeier, J. Wanner, Surf. Sci., 2000, 454-456, 305
- J.M. Gottfried, K.J. Schmidt, S.L.M. Schroeder,
 K. Christmann, *Surf. Sci.*, 2003, **525**, 184
- J.M. Gottfried, K.J. Schmidt, S.L.M. Schroeder,
 K. Christmann, *Surf. Sci.*, 2003, **525**, 197
- 75 D.H. Parker, B.E. Koel, Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films, 1990, 8, 2585
- 76 N. Saliba, D.H. Parker, B.E. Koel, Surf. Sci., 1998, 410, 270
- 77 A.S.K. Hashmi, Gold Bull., 2004, 37, 51
- 78 S. Ivanova, C. Petit, V. Pitchon, Gold Bull., 2006, 39, 3
- 79 F. Cárdenas-Lizana, S. Gómez-Quero, N. Perret, M.A. Keane, *Gold Bull.*, 2009, **42**, 124
- 80 S.A. Nikolaev, V.V. Smirnov, Gold Bull., 2009, 42, 182
- 81 C.D. Pina, E. Falletta, M. Lo Faro, M. Pasta, M. Rossi, *Gold Bull.*, 2009, **42**, 27
- 82 M.S. Chen, D.W. Goodman, Science, 2004, 306, 252
- 83 C. Zhang, A. Michaelides, D.A. King, S.J. Jenkins, J. Chem. Phys., 2008, **129**, 194708
- 84 C.J. Weststrate, R. Westerström, E. Lundgren, A. Mikkelsen, J.N. Andersen, A. Resta, J. Phys. Chem. C, 2009, 113, 724
- 85 N.C. Hernández, R. Grau-Crespo, N.H. De Leeuw, J.F. Sanz, Phys. Chem. Chem. Phys., 2009, 11, 5246
- M.L. Kimble, N.A. Moore, A.W. Castleman Jr, C. Bürgel,
 R. Mitrić, V. Bonačić-Koutecký, *European Physical Journal* D, 2007, 43, 205
- 87 L.M. Molina, B. Hammer, J. Chem. Phys., 2005, 123, 1
- A. Fielicke, G. Von Helden, G. Meijer, B. Simard,
 D.M. Rayner, *J. Phys. Chem. B*, 2005, **109**, 23935
- 89 Q. Sun, P. Jena, Y.D. Kim, M. Fischer, G. Ganteför, J. Chem. Phys., 2004, **120**, 6510
- 90 X. Wu, L. Senapati, S.K. Nayak, A. Selloni, M. Hajaligol, J. Chem. Phys., 2002, **117**, 4010
- J. Hagen, L.D. Socaciu, M. Elijazyfer, U. Heiz,
 T.M. Bernhardt, L. Wöste, *Phys. Chem. Chem. Phys.*, 2002,
 4, 1707
- 92 P. Schwerdtfeger, M. Lein, R.P. Krawczyk, C.R. Jacob, J. Chem. Phys., 2008, **128**, 124302
- 93 A.M. Joshi, W.N. Delgass, K.T. Thomson, J. Phys. Chem. C, 2007, **111**, 11424
- 94 P. Frondelius, H. Häkkinen, K. Honkala, *New J. Phys.*, 2007, 9, 339
- 95 S. Chrétien, H. Metiu, J. Chem. Phys., 2007, 126, 104701
- 96 A. Vittadini, A. Selloni, J. Chem. Phys., 2002, 117, 353
- 97 J.E. Macur, R.W. Vook, Thin Solid Films, 1980, 66, 371
- 98 G.A. Evangelakis, G.C. Kallinteris, N.I. Papanicolaou, Surf. Sci., 1997, **394**, 185

- 99 W. Wallauer, T. Fauster, Surf. Sci., 1995, 331-333, 731
- 100 T.C.Q. Noakes, P. Bailey, *Thin Solid Films*, 2001, **394**, 15
- 101 A. Politano, G. Chiarello, Gold Bull., 2009, 42, 195
- 102 S. Dahl, A. Logadottir, C.J.H. Jacobsen, J.K. Norskov, Applied Catalysis a-General, 2001, **222**, 19
- 103 I. Hannus, I. Palinko, G. Tasi, A. Beres, I. Kiricsi, Bulletin of the Chemical Society of Japan, 1996, 69, 1429
- H.N. Evin, G. Jacobs, J. Ruiz-Martinez, G.A. Thomas,
 B.H. Davis, *Catal. Lett.*, 2008, **120**, 166
- J.A. Norcross, C.P. Slichter, J.H. Sinfelt, *Catal. Today*, 1999, 53, 343
- 106 J.G. Chen, M.D. Weisel, F.M. Hoffmann, R.B. Hall, Catalytic Selective Oxidation, 1993, 523, 133
- 107 B.E. Spiewak, P. Levin, R.D. Cortright, J.A. Dumesic, *J. Phys. Chem.*, 1996, **100**, 17260
- 108 R. Schenkel, A. Jentys, S.F. Parker, J.A. Lercher, *J. Phys. Chem. B*, 2004, **108**, 15013
- N. Alsarraf, J.T. Stuckless, D.A. King, *Nature*, 1992, **360**, 243
- 110 C.Y. Tang, H.C. Allen, J. Phys. Chem. A, 2009, 113, 7383
- A. Politano, R.G. Agostino, E. Colavita, V. Formoso, G. Chiarello, Surf. Sci., 2007, 601, 2656
- A. Politano, R.G. Agostino, E. Colavita, V. Formoso,
 G. Chiarello, J. Nanosci. Nanotechnol., 2009, 9, 3932
- S. Achilli, M.I. Trioni, E.V. Chulkov, P.M. Echenique,
 V. Sametoglu, N. Pontius, A. Winkelmann, A. Kubo, J. Zhao,
 H. Petek, *Phys. Rev. B*, 2009, **80**, 245419
- 114 A. Politano, V. Formoso, G. Chiarello, *J. Phys. Chem. C*, 2008, **112**, 17772
- 115 G. Fratesi, Phys. Rev. B, 2009, 80, 045422
- 116 A. Politano, V. Formoso, R.G. Agostino, E. Colavita, G. Chiarello, *J. Chem. Phys.*, 2008, **128**, 074703
- 117 Z.P. Liu, P. Hu, J. Am. Chem. Soc., 2001, 123, 12596
- 118 S.J. Jenkins, D.A. King, *J. Am. Chem. Soc.*, 2000, **122**, 10610
- 119 A. Politano, A.R. Marino, G. Chiarello, *Chem. Phys.*, 2010, **367**, 148
- A. Politano, A.R. Marino, G. Chiarello, J. Chem. Phys., 2010, 132, 044706
- 121 A. Politano, G. Chiarello, Chem. Phys. Lett., 2010, 494, 84
- 122 M.G. Blaber, M.D. Arnold, M.J. Ford, J. Phys.: Cond. Matt., 2009, 21
- 123 L. Belpassi, F. Tarantelli, A. Sgamellotti, H.M. Quiney, *J. Phys. Chem. A*, 2006, **110**, 4543
- 124 M.V. Knat'ko, M.N. Lapushkin, V.I. Paleev, *Technical Physics*, 2005, **50**, 498
- 125 A. Stangassinger, A.M. Knight, M.A. Duncan, *J. Phys. Chem. A*, 1999, **103**, 1547
- 126 M.V. Knat'ko, V.I. Paleev, M.N. Lapushkin, *Technical Physics*, 1998, **43**, 1231
- 127 M.V. Knat'ko, M.N. Lapushkin, V.I. Paleev, *Technical Physics*, 1998, **43**, 1235

- 128 M.V. Knat'ko, V.I. Paleev, M.N. Lapushkin, *Physics of Low-Dimensional Structures*, 1998, **1998**, 85
- 129 G.H. Grosch, K.J. Range, Journal of Alloys and Compounds, 1996, 233, 30
- 130 J.V. Barth, R.J. Behm, G. Ertl, Surf. Sci., 1995, 341, 62
- 131 U. Heiz, A. Vayloyan, E. Schumacher, C. Yeretzian,
 M. Stener, P. Gisdakis, N. Rösch, *J. Chem. Phys.*, 1996, **105**, 5574
- 132 A. Politano, R.G. Agostino, E. Colavita, V. Formoso,L. Tenuta, G. Chiarello, *J. Phys. Chem. C*, 2008, **112**, 6977
- A. Politano, R.G. Agostino, E. Colavita, V. Formoso,
 G. Chiarello, *Phys. Status Solidi-Rapid Res. Lett. (RRL)*,
 2008, 2, 86
- 134 A. Politano, G. Chiarello, V. Formoso, R.G. Agostino,
 E. Colavita, *Phys. Rev. B*, 2006, **74**, 081401
- 135 A. Politano, V. Formoso, G. Chiarello, J. Phys. Chem. C, 2009, **113**, 316
- L. Savio, L. Vattuone, M. Rocca, *Appl. Phys. A*, 2007, **87**, 399
- 137 V. Chis, B. Hellsing, G. Benedek, M. Bernasconi, E.V. Chulkov, J.P. Toennies, *Phys. Rev. Lett.*, 2009, **103**, 069902
- 138 V. Chis, B. Hellsing, G. Benedek, M. Bernasconi, E.V. Chulkov, J.P. Toennies, *Phys. Rev. Lett.*, 2008, **101**, 206102
- 139 B.M. Hall, D.L. Mills, M.H. Mohamed, L.L. Kesmodel, *Phys. Rev. B*, 1988, **38**, 5856
- 140 M.H. Mohamed, L.L. Kesmodel, B.M. Hall, D.L. Mills, *Phys. Rev. B*, 1988, **37**, 2763
- 141 C. Astaldi, P. Rudolf, S. Modesti, *Solid State Commun.*, 1990, 75, 847
- 142 P. Rudolf, C. Astaldi, G. Cautero, S. Modesti, *Surf. Sci.*, 1991, 251-252, 127
- 143 A. Politano, V. Formoso, G. Chiarello, J. Phys.: Condens. Matter, 2009, 21, 264006
- 144 A. Politano, V. Formoso, R.G. Agostino, E. Colavita,
 G. Chiarello, *Phys. Rev. B*, 2007, **76**, 233403
- 145 R. Davis, R. Toomes, D.P. Woodruff, O. Schaff, V. Fernandez, K.M. Schindler, P. Hofmann, K.U. Weiss, R. Dippel, V. Fritzsche, A.M. Bradshaw, *Surf. Sci.*, 1997, **393**, 12
- 146 A. Politano, V. Formoso, G. Chiarello, *Appl. Surf. Sci.*, 2008, 254, 6854
- 147 A. Politano, R.G. Agostino, V. Formoso, G. Chiarello, *Chemphyschem*, 2008, **9**, 1189
- 148 A. Politano, V. Formoso, G. Chiarello, Surf. Sci., 2008, 602, 2096
- 149 A. Politano, V. Formoso, G. Chiarello, J. Chem. Phys., 2008, 129, 164703
- 150 A. Politano, V. Formoso, G. Chiarello, *Superlattices Microstruct.*, 2009, **46**, 10
- 151 T.A. Baker, C.M. Friend, E. Kaxiras, *J. Phys. Chem. C*, 2009, 113, 3232
- 152 T. Sueyoshi, T. Sasaki, Y. Iwasawa, Surf. Sci., 1996, 365, 310
- 153 G. Benedek, F.B. de Mongeot, U. Valbusa, M. Rocca, *Europhysics Letters*, 2001, **53**, 544

- 154 H. Ibach, D.L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations* (Academic Press, San Francisco, 1982).
- 155 J.D. Stiehl, T.S. Kim, S.M. McClure, C.B. Mullins, *J. Am. Chem. Soc.*, 2004, **126**, 1606
- 156 V. Bondzie, S. Parker, C. Campbell, *Catal. Lett.*, 1999, **63**, 143
- G. Mills, M.S. Gordon, H. Metiu, *J. Chem. Phys.*, 2003, **118**, 4198
- 158 D.J. Gorin, F.D. Toste, Nature, 2007, 446, 395

- 159 Z.Y. Li, N.P. Young, M. Di Vece, S. Palomba, R.E. Palmer, A.L. Bleloch, B.C. Curley, R.L. Johnston, J. Jiang, J. Yuan, *Nature*, 2008, **451**, 46
- 160 C.H. Christensen, J.K. Nørskov, Science, 2010, 327, 278
- D. Matthey, J.G. Wang, S. Wendt, J. Matthiesen, R. Schaub,
 E. Lægsgaard, B. Hammer, F. Besenbacher, *Science*, 2007,
 315, 1692
- 162 P.J. Roach, W.H. Woodward, A.W. Castleman Jr, A.C. Reber, S.N. Khanna, *Science*, 2009, **323**, 492
- 163 A. Wittstock, V. Zielasek, J. Biener, C.M. Friend, M. Bäumer, Science, 2010, **327**, 319