ELSEVIER
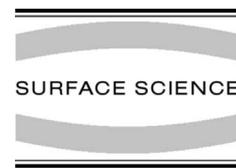
Surface Science Letters

# Selectivity of bond-breaking in electron-induced dissociation of hydrocarbon films on Au surfaces

Denis Syomin, Bruce E. Koel *

*Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0482, USA*

Received 4 June 2001; accepted for publication 18 June 2001

## Abstract

Electron-induced dissociation (EID) processes in organic and polymer films are important in a variety of applications. One scientific issue concerns the selectivity of low-energy electron bombardment to cleave a single C–H bond in hydrocarbon condensed films or adsorbed layers. We have undertaken combined TPD and FT-IRAS studies to identify and determine the purity of the surface species produced by EID of cyclohexane and benzene films on Au(1 1 1). Experimental evidence strongly supports a conclusion that EID of cyclohexane and benzene monolayer and multilayer films using incident electrons with an energy of 30 eV can be used to cleave a single C–H bond and produce a single chemisorbed product with high selectivity. An important consequence of these observations is that a variety of adsorbed hydrocarbon intermediates on Au(1 1 1) and other metal surfaces can be prepared in this manner, spectroscopically characterized, and used in studies to advance the understanding of chemical bonding, reactions and catalysis at surfaces. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Gold; Infrared absorption spectroscopy; Thermal desorption; Electron bombardment; Aromatics; Alkanes; Alkynes

## 1. Introduction

The interactions of electrons with organic adsorbed layers and polymer films play an important role in a variety of applications [1,2]. Of particular interest to us is the potential for using low-energy, electron-induced dissociation (EID) to cleanly and selectively prepare reactive, hydrocarbon species at transition metal surfaces. These species are of interest as intermediates in surface science studies of elementary processes in catalysis over metal surfaces and in controlling the electronic properties of metal–organic interfaces in microelectronic applications.

Under UHV conditions, many hydrocarbons of interest are reversibly adsorbed, i.e., they cannot be thermally "activated" to dissociate and form strong covalent bonds to metal atoms at the surface. A variety of non-thermal methods have been explored, including trapping incident ions and radicals [3,4] and using reactive precursors and synthesis reactions on the surface [5], and PID, EID and CID [6–9] to activate stable molecules. A key issue in all of these methods is the efficiency and selectivity to prepare well-defined, surface-bound species.

---

* Corresponding author. Tel.: +1-213-740-7036; fax: +1-213-740-2701.
   *E-mail address:* koel@chem1.usc.edu (B.E. Koel).

The utility of EID with physisorbed molecules on Ag was pointed out some time ago in studies by White and coworkers [8,10–12]. Our contribution was to show that one could use EID of physisorbed multilayers on reactive transition metal substrates like Pt [13] that formed chemisorbed hydrocarbon adlayers. Fragments produced in EID of these multilayer films diffuse to the surface and bond there [14], where efficient relaxation of subsequent electron-induced excitation greatly inhibits further EID reactions within this bound layer. Thus, we were able to prepare a monolayer of cyclohexyl (c-$C_6H_{11}$) species on Pt(1 1 1) and two Pt–Sn surface alloys by the activation of cyclohexane (c-$C_6H_{12}$) using EID at 30 eV [15]. Using this technique, we were able to establish structure–reactivity correlations on Pt–Sn alloys in the cyclohexane (c-$C_6H_{12}$) to benzene (c-$C_6H_6$) conversion reaction. Similar studies of the reactions of chemisorbed cycloalkyl groups were also carried after preparation by using EID to activate $C_{5-8}$ cycloalkane multilayers on Pt(1 1 1) and Pt–Sn alloys [16].

While the chemistry of these cycloalkyl monolayers seems to be fairly clean, and the previous HREELS data on the formation of cyclohexyl is supportive, how selective is EID really? This issue must be addressed. Can we cleanly produce cyclohexyl using EID of physisorbed cyclohexane? More generally, can EID be used to cleanly and selectively prepare hydrocarbon intermediates at reactive transition metal surfaces? What is the selectivity of low-energy electron bombardment to cleave a single C–H bond in condensed or adsorbed hydrocarbon films?

Our approach to answer these questions is to utilize a relatively inert metal surface, i.e., Au(1 1 1), to minimize the possible influence of subsequent thermal reactions after generating a transient intermediate by EID, and to use molecular-level surface probes – Fourier transform infrared reflection-absorption spectroscopy (IRAS) and temperature programmed desorption (TPD) mass spectrometry. We demonstrate that cyclohexyl (c-$C_6H_{11}$) and phenyl (c-$C_6H_5$) groups on Au(1 1 1) at 90 K may be cleanly produced by 30 eV-EID of cyclohexane and benzene monolayer films, respectively.

## 2. Experimental details

The experiments were performed in a UHV chamber with a base pressure of $6 \times 10^{-10}$ Torr and equipped for Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), TPD and FT-IRAS studies. The Au(1 1 1) crystal could be resistively heated to 1000 K and cooled to 87 K by direct contact of a copper block on the sample holder with liquid nitrogen. The crystal temperature was measured by a chromel–alumel thermocouple pressed tightly and directly into a small hole drilled in the edge of the crystal.

The Au(1 1 1) surface was cleaned by cycles of Ar$^+$ ion sputtering (0.5 keV, $6 \times 10^{-5}$ Torr) at 650 K for 12 min and annealing at 1000 K for 20 min in UHV. This procedure resulted in a clean, well-ordered Au(1 1 1) surface which showed the ($\sqrt{3} \times$ 22) reconstruction of the surface [17] in LEED. No surface carbon was detected by AES.

TPD measurements were made with the sample placed in line-of-sight of the mass spectrometer ionizer at a location of 2 mm in front of the entrance aperture to a shield covering the ionizer.

IRAS studies were carried out at a grazing incidence angle of ~86°. Either a Mattson Galaxy® 6020 or an Infinity® 60M FT-IR spectrometer was used for collecting the IR data. A narrow-band, liquid-nitrogen cooled, mercury cadmium telluride (MCT) detector was used. Typically spectra were taken with the spectrometer resolution set to 4 cm$^{-1}$ and by averaging 1000 or 2000 scans. All reported IRAS spectra were taken at 90 K and ratioed against the clean Au(1 1 1) surface background.

EID experiments were performed by using a variable-energy electron gun (5–1000 eV, Kimball Physics, Model FRA $2 \times 12$). During the experiments electron beam was defocused over the crystal surface, the incident electron beam energy was 30 eV and the incident beam current was 10–11 μA, as measured with the sample biased by +125 V. The electron beam profile was measured in previous studies using a Faraday cup to have a full width at half maximum equal to the crystal diameter, so that the flux varies across the surface by atmost a factor of two [18].

$C_6H_{12}$ and $C_6H_6$ coverages herein are referenced to $\theta = 1$ monolayer (ML) for those coverage that

corresponds to saturation of the most strongly bound $C_6H_{12}$ and $C_6H_6$ TPD peaks on Au(1 1 1). The $C_6H_{12}$ and $C_6H_6$ exposures required to form this monolayer coverages were determined in TPD experiments.

## 3. Results and discussion

### 3.1. EID of a benzene monolayer on Au(1 1 1)

Fig. 1 shows TPD spectra from a benzene monolayer on Au(1 1 1) at 90 K, taken before and after exposure to 30-eV electrons during EID. Benzene is weakly bound to the Au(1 1 1) surface ($\sim$14.7 kcal/mol), desorbing in a peak at 239 K at low coverages and at 202 K near monolayer coverage [20]. Multilayer benzene desorption has an onset at $\sim$140 K, and a small amount of this phase can be seen desorbing in Fig. 1(a). No other products were observed in TPD and no carbon

was detected on the surface by AES after TPD; benzene is completely reversibly adsorbed. After exposure of the benzene monolayer to electrons, changes occur in TPD spectra as shown in Fig. 1(a) and (b). The benzene desorption peak becomes narrower and decreases in size with increasing electron exposure. At the same time, biphenyl evolution can be detected in a peak near 400 K. The amount of biphenyl that is desorbed increases the electron dose [20], and reaches a yield of $0.25\theta^{\mathrm{sat}}$ ($\theta^{\mathrm{sat}}_{C_{12}H_{10}} = 0.084$ ML, defined relative to the Au surface atom density on Au(1 1 1)). Benzene and biphenyl were the only TPD products detected after EID.

We explain the changes in the TPD spectra by the chemical reactions occurring on the surface (Scheme 1).

The IRAS spectrum of the benzene monolayer on Au(1 1 1) exhibits only one vibrational band at 682 cm$^{-1}$ arising from the CH out-of-plane bending mode [20]. The dynamic dipoles of the other
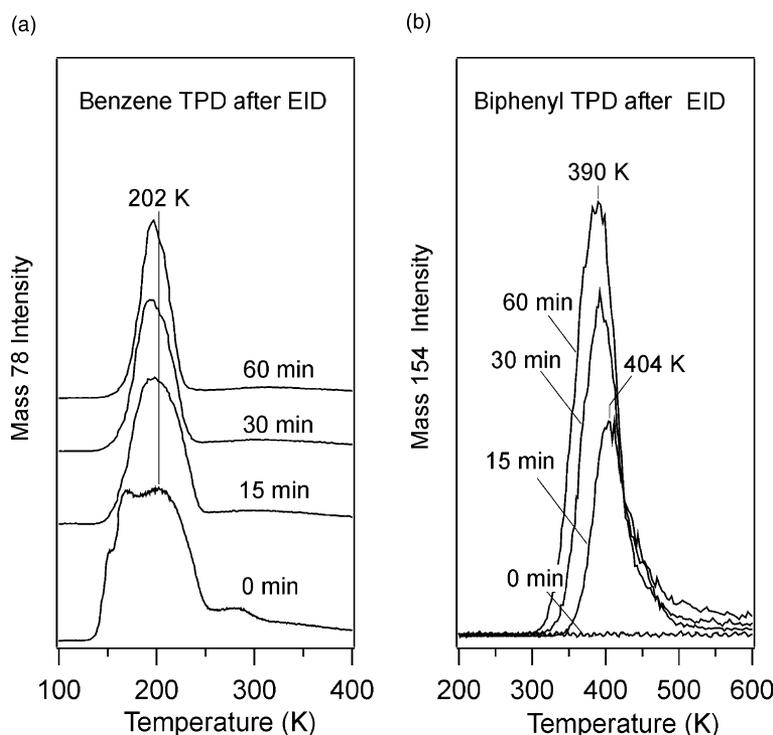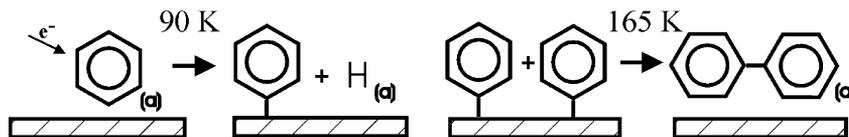


(a)

(b)

Benzene TPD after EID

Mass 78 Intensity

202 K

60 min

30 min

15 min

0 min

Biphenyl TPD after EID

Mass 154 Intensity

390 K

60 min

30 min

404 K

15 min

0 min

Temperature (K)

Fig. 1. (a) Benzene ($C_6H_6$) and (b) biphenyl ($C_{12}H_{10}$) TPD spectra after a $C_6H_6$ monolayer on Au(1 1 1) at 90 K was exposed to 30-eV electrons ($I_i = 10$ μA).

Scheme 1.

modes are screened by the surface according to the surface dipole-selection rule [19] because the benzene molecules in the monolayer adopt a "flat-lying" orientation with the ring plane parallel to the surface [20]. After electron bombardment in EID, the IRAS spectra exhibited four new vibrational modes, as shown in Fig. 2. The position and intensity of these bands correlate well with those observed in the IR spectrum of phenyl radicals in an Ar matrix [21,22]. These bands are assigned to C–C (991, 1459, 1557 cm$^{-1}$) and C–H (3055 cm$^{-1}$) in-plane stretching modes of phenyl groups adsorbed on the Au(1 1 1) surface [20]. The intense mode at 682 cm$^{-1}$ in the top spectrum is due to the out-of-plane C–H bending mode of benzene molecules still present on the surface. Based on the

surface selection rule and symmetry analysis of the phenyl group vibrational modes detected in the IR spectra, we deduced that the phenyl group was adsorbed with the molecular plane perpendicular to the surface plane, but with a tilt of the molecular $z$ axis towards the surface [20]. IRAS also showed that heating the surface above 165 K leads to phenyl group coupling and the formation of biphenyl, adsorbed in a "flat-lying" orientation on the surface. Therefore, IRAS and TPD data clearly show that electron bombardment at 30 eV of a 1-ML benzene film on Au(1 1 1) leads to clean dissociation of a single C–H bond and the formation of adsorbed phenyl groups.

### 3.2. EID of a cyclohexane monolayer on Au(1 1 1)

Electron bombardment of a cyclohexane monolayer can nearly completely eliminate cyclohexane desorption from the chemisorbed state, as shown in Fig. 3(a). At the same time, new desorption states appear in the TPD spectra (Fig. 3(a) and (b)) for cyclohexane at 273 K along with cyclohexene at 216 and 273 K. Cyclohexane and cyclohexene are the only TPD products detected in EID experiments and no carbon was detected on the surface by AES after TPD. This TPD data can be easily explained if the EID of cyclohexane leads to the formation of adsorbed cyclohexyl groups. These undergo thermal reaction during TPD via disproportionation at ~273 K to cause coincident cyclohexane and cyclohexene desorption peaks (Scheme 2). Cyclohexene desorption at 216 K is due to a desorption-rate limited process after dehydrogenation of cyclohexyl groups that occurs at $T < 216$ K.

We would expect there to be similarity between the IR spectra of adsorbed cyclohexane molecules and cyclohexyl groups, and so we plot the IRAS spectra of these molecules together for comparison
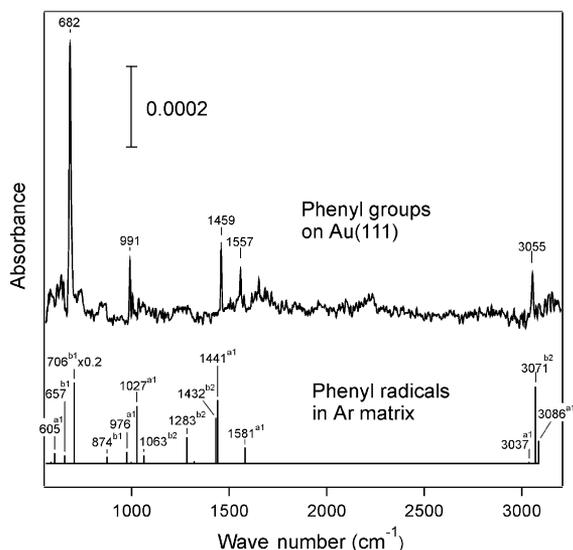


Fig. 2. Top: IRAS spectrum after a C$_6$H$_6$ monolayer on Au(1 1 1) at 90 K was exposed to 30-eV electrons ($I_i = 10$ μA for 45 min to give $2.14 \times 10^{17}$ electrons/cm$^2$). Bottom: Diagram of the IR spectrum of phenyl radicals in an Ar matrix, constructed using the band positions and intensities reported in Ref. [21].
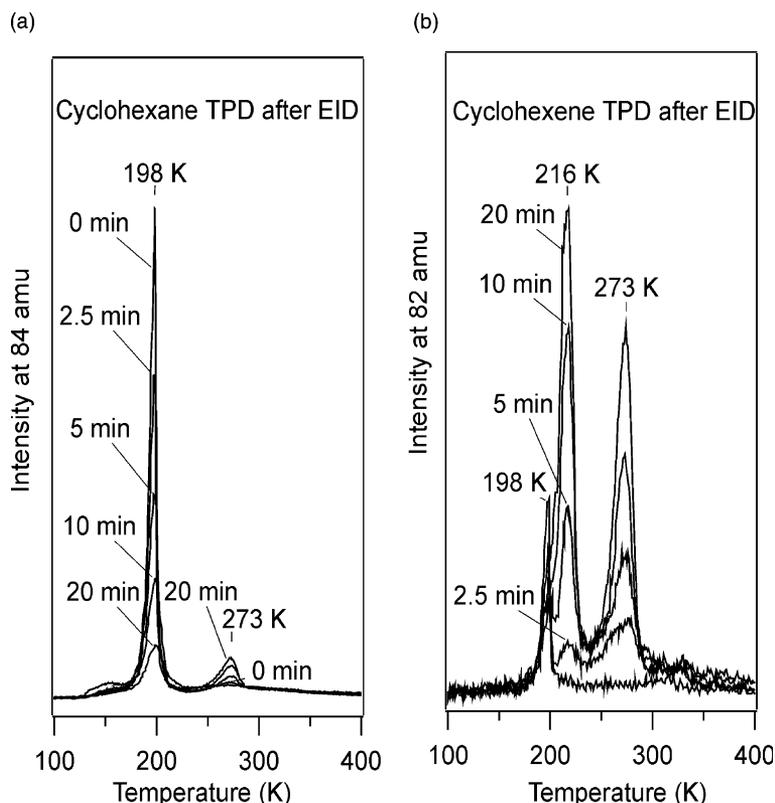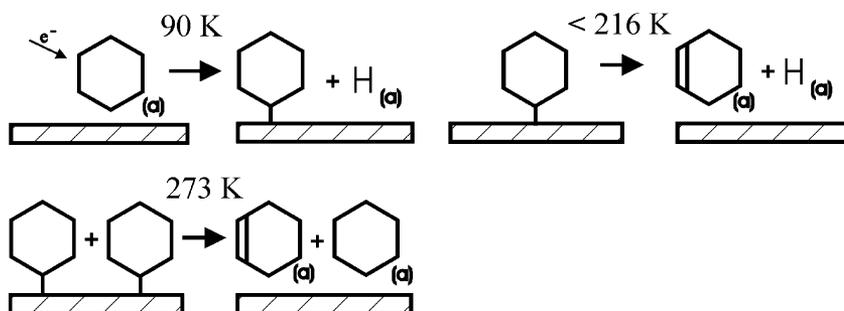
Fig. 3. (a) Cyclohexane (c-$C_6H_{12}$) and (b) cyclohexene (c-$C_6H_{10}$) TPD spectra after a c-$C_6H_{12}$ monolayer on Au(1 1 1) at 90 K was exposed to 30-eV electrons ($I_i = 11$ μA).



Scheme 2.

in Fig. 4. We also provide the IRAS spectra of a 0.5-ML cyclohexene adlayer as well, because a significant amount of cyclohexene forms on the surface below 216 K and it is important to know if this happens during the electron exposure at 90 K or during the subsequent heating in TPD. We chose IRAS spectra of cyclohexane and cyclohexene at 0.5 ML coverage for comparison here,
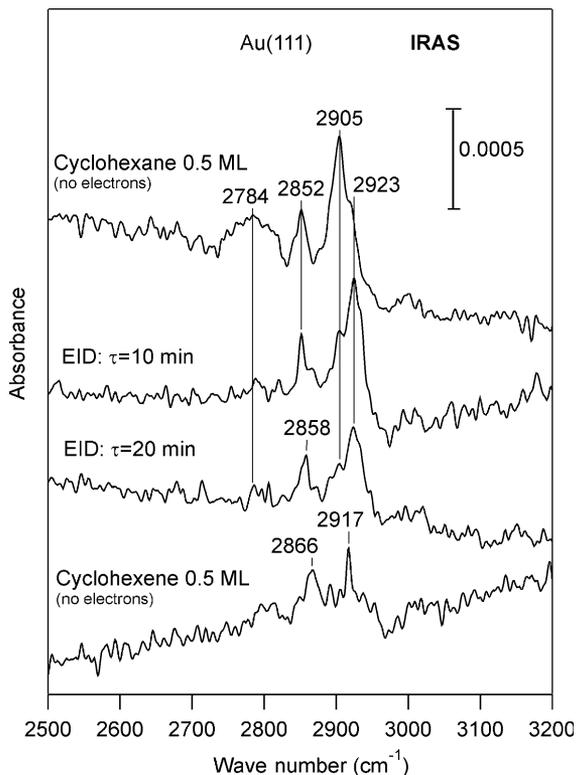
Fig. 4. IRAS spectra of 0.5-ML cyclohexane, 1-ML cyclohexene, and 1-ML cyclohexane after exposure to 30-eV electrons ($I_i = 11$ μA).

since we know that the surface coverage of cyclohexane and cyclohexyl is 0.39 and 0.41 ML respectively after a 10 min exposure of electrons in EID, and the surface coverage of cyclohexane and cyclohexyl is 0.2 and 0.58 ML, respectively, after 20 min of electron bombardment in EID [23]. The IRAS spectra for 0.5 ML of cyclohexane adsorbed on Au(1 1 1) exhibits four bands: 2923 and 2905 cm$^{-1}$ due to asymmetric C–H stretching ($\nu_{as}$CH), 2852 cm$^{-1}$ due to symmetric C–H stretching ($\nu_s$CH) and 2784 cm$^{-1}$ due to the so called "soft" C–H stretching mode. The origin of the "soft" mode comes from the interaction of hydrogens projecting directly into the surface, leading to the strong shift of the C–H stretching frequency to the red and possibly C–H bond weakening. The presence of such a "soft" band is a common feature of the IR spectra of cyclohexane adsorbed on metal surfaces [24–26]. The IRAS spectra of 0.5

ML of cyclohexene exhibits two vibrational bands at 2916 and 2866 cm$^{-1}$ due to aliphatic C–H stretching modes. The olefinic C–H stretching mode at 2935 cm$^{-1}$ is screened by the surface at monolayer and submonolayer coverages but may be observed in thicker cyclohexene films [23]. IRAS spectra taken after the 1-ML cyclohexane film on Au(1 1 1) was exposed to electrons is quite similar to cyclohexane spectra taken without electron exposure. The spectra exhibits three vibrational bands: 2858 cm$^{-1}$ due to $\nu_s$(CH) modes, and 2905 and 2923 cm$^{-1}$ due to $\nu_s$(CH) modes. The intensity of the $\nu_s$(CH) band of the cyclohexane monolayer does not change after electron exposure, but the frequency shifts slightly to the red from 2852 to 2858 cm$^{-1}$. Another change that occurred in the cyclohexane spectra after electron exposure is in the relative intensities of the $\nu_{as}$(CH) modes at 2905 and 2923 cm$^{-1}$, such that the band at 2923 cm$^{-1}$ becomes the most intense after electron exposure. The main change that occurs in the cyclohexane IRAS spectra obtained after electron exposure is the disappearance of the "soft" mode in the cyclohexane IRAS spectra. This is strong evidence for a change in the orientation of the molecule in such a way that no hydrogen atoms are projected directly into the surface. We propose that this change in orientation is a result of the change in the nature of molecular bonding to the surface, from a weak physisorption interaction that leads to a somewhat "flat-lying" geometry for the cyclohexane molecules to a covalent Au–C σ bond that leads to a relatively "upright" geometry for adsorbed cyclohexyl groups. Phenyl groups also adsorb on the Au(1 1 1) surface with the molecular ring-plane perpendicular to the surface plane [20]. The IRAS data can be best explained by the formation of surface species that highly resemble cyclohexane molecules, but that have a different adsorption geometry. We can also exclude the possibility of cyclohexene formation during EID since the vibrational fingerprints of authentic, dosed cyclohexene do not match well that of the cyclohexane EID products. Along with the TPD data, this leads us to conclude that bombardment of a cyclohexane monolayer film adsorbed on Au(1 1 1) at 90 K with 30 eV energy electrons leads to the selective cleavage of one C–H bond in

cyclohexane molecules to cleanly form adsorbed cyclohexyl groups on the surface.

## 4. Conclusions

EID at 30 eV is an efficient and selective process for cleaving a single C–H bond in small hydrocarbon molecules in condensed phases. Thus, EID can provide sufficient molecular-level control to enable probes of the structure, bonding, and reactions of small, symmetrical hydrocarbon intermediates at metal surfaces, and presumably in other systems too. These conclusions are based on experiments that show that EID of a benzene monolayer film adsorbed on a Au(1 1 1) surface at 90 K leads to the dissociation of a single C–H bond in a benzene molecule and subsequent formation of adsorbed phenyl groups. Phenyl groups undergo hydrogenation to benzene on Au(1 1 1) near 100 K and coupling reactions to form adsorbed biphenyl molecules at 165 K. EID of a cyclohexane monolayer film on Au(1 1 1) at 90 K leads to cleavage of a single C–H bond and formation of adsorbed cyclohexyl groups. Cyclohexyl groups dehydrogenate to cyclohexene on Au(1 1 1) at below 216 K and undergo extensive disproportionation reaction to form cyclohexane and cyclohexene at 275 K.

## Acknowledgements

## References

[1] T. Abe, K. Moriizumi, Y. Ochiai, N. Saitou, T. Takigawa, N. Saitou, in: K. Suzuki, S. Matsui, Y. Ochiai (Eds.), Sub-Half-Micron Lithography for ULSIS, Cambridge University Press, Cambridge, 2000, p. 107.
[2] A. Hatzor, P.S. Weiss, Science 291 (2001) 1019.
[3] X.D. Peng, R. Viswanathan, G.H. Smude Jr., P.C. Stair, Rev. Sci. Instr. 63 (1992) 3930.
[4] T.J. Chuang, Y.L. Chan, P. Chuang, R. Klauser, J. Electr. Spectrosc. Rel. Phenom. 98–99 (1999) 149.
[5] C.-M. Chiang, B.E. Bent, Surf. Sci. 279 (1992) 79.
[6] G.J. Szulczevski, J.M. White, Surf. Sci. 399 (1998) 305.
[7] R. Franchy, Rep. Prog. Phys. 63 (1998) 691.
[8] X.-L. Zhou, M.E. Castro, J.M. White, Surf. Sci. 238 (1990) 215.
[9] B.E. Bent, Chem. Rev. 96 (1996) 1361 and references therein.
[10] J.M. White, Langmuir 10 (1994) 3946.
[11] D.J. Alberas-Sloan, J.M. White, Surf. Sci. 365 (1996) 212.
[12] X.-L. Zhou, A.L. Schwaner, J.M. White, J. Am. Chem. Soc. 115 (1993) 4309.
[13] C. Xu, B.E. Koel, Surf. Sci. 292 (1993) L803.
[14] L. Tsai, B.E. Koel, J. Phys. Chem. 101 (1997) 4781.
[15] C. Xu, B.E. Koel, J. Phys. Chem. 98 (1997) 585.
[16] L. Tsai, B.E. Koel, Langmuir 14 (1998) 1290.
[17] M.A. Van Hove, R.J. Koestner, P.C. Stair, J.P. Biberian, L.L. Kesmodel, I. Bartos, G.A. Somorjai, Surf. Sci. 103 (1981) 189.
[18] Y.-L. Tsai, Ph.D. Thesis, University of Southern California, 1996.
[19] B.E. Hayden, in: J.T. Yates Jr., T.E. Madey (Eds.), Vibrational Spectroscopy of Molecules on Surfaces, Plenum Press, New York, 1987, p. 267.
[20] D. Syomin, J. Kim, B.E. Koel, G.B. Ellison, J. Phys. Chem., in press.
[21] J.G. Radziszevski, M.R. Nimlos, P.R. Winter, G.B. Ellison, J. Am. Chem. Soc. 118 (1996) 7400.
[22] A.V. Friderichsen, J.L.G. Radziszevski, M.R. Nimlos, P.R. Winter, D.C. Dayton, D.E. David, G.E. Ellison, J. Am. Chem. Soc. 123 (2001) 1977.
[23] D. Syomin, B.E. Koel, Surf. Sci. 490 (2001) 265.
[24] R. Raval, M.A. Chesters, Surf. Sci. 219 (1989) L505.
[25] R. Raval, S.F. Parker, M.A. Chesters, Surf. Sci. 289 (1993) 227.
[26] A.V. Teplyakov, B.E. Bent, J. Eng Jr., J.G. Chen, Surf. Sci. 399 (1995) L342.