



UHV Surface Science

Customer Contributions:

Reactions of ethanol on Ru(0001)

J. M. Sturm | Materials innovation institute M2i

Challenges and prospects for developing CdS/CdTe substrate solar cells on Mo foils

Benjamin L. Williams | Eindhoven University of Technology

Electron attachment to a model peptide, N-methylformamide

M. Michele Dawley & Sylwia Ptasińska | University of Notre Dame

Chasing Stardust

Prof Martin McCoustra & Alexander Rosu-Finsen | Heriot Watt University

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A very big thank you to all who have contributed:



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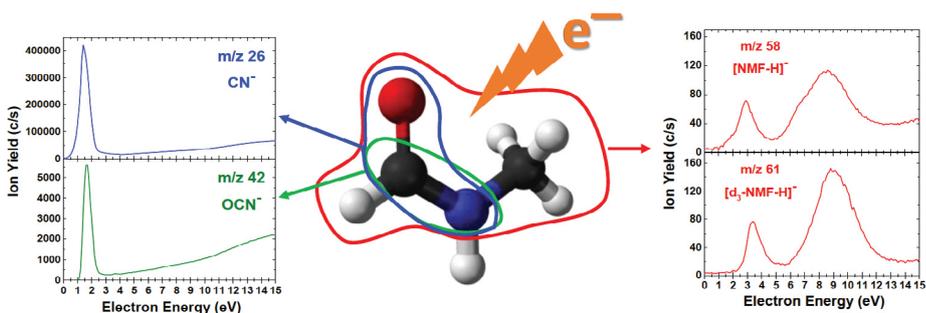


Electron attachment to a model peptide, N-methylformamide, using a Hiden IDP-QMS

Significance: Dissociative electron attachment (DEA) is an electron-induced fragmentation process, occurring at low energies (<15 eV), that is of interest to the fields of radiation chemistry, physics, radiation therapy, astrochemistry, and materials and surface science. N-methylformamide (HC(O)NHCH_3 , denoted as NMF), a simple amide containing the peptide linkage, mimics a possible scenario that could happen locally in peptides. Low-energy secondary electrons (<20 eV) are primarily formed within cells during radiation cancer therapies; thus, studies of electron interactions with biomolecules, such as NMF, have become vital to understand the short- and long-term effects of such therapies. One eventual aim is the understanding of DEA in relation to larger peptides and proteins, which is valuable to many fields, specifically radiation therapy research.

Summary: Having purchased two Hiden Analytical Ion Desorption Probe (IDP) Quadrupole Mass Spectrometers (QMS), the Ptasinska lab is uniquely equipped for DEA studies. This investigation used a new and recently optimized experimental high vacuum chamber (base pressure $\sim 1 \times 10^{-8}$ mbar) that was designed and built at the Notre Dame Radiation Laboratory (NDRL). Using this unique system, crossed molecular beam/low-energy electron experiments can detect anions, cations, radical, and neutral species using mass spectrometric detection with the IDP-QMS from Hiden. The IDP-QMS system was used for gas-phase detection of anions resulting from the DEA to NMF and N-methyl- d_3 -formamide (d_3 -NMF) using the internal oxide-coated iridium filament as the electron source in the negative Residual Gas Analyzer mode. Anions formed upon electron bombardment in the ion source were then detected by an ion counting detector in the IDP-QMS. Anion mass spectra were obtained at several electron energies, and then energy scans (0-15 eV) were performed for each observed anion (dwell time - 1 s, energy step - 0.1 eV) using MASsoft version 7 Professional software by Hiden. An average electron energy resolution of ~ 500 meV at an electron current of 2.0 μA was determined from the SF_6^- signal at 0 eV.

As shown in the figure, the dominant fragmentation pathways from the DEA to NMF involved the formation of CN^- and OCN^- near 1.5 eV produced from the electron capture by the π^* orbital of C=O combined with the scission of the N- CH_3 bond and simultaneous formation of a C=N π bond. We also observed the [Parent - H] $^-$ yields induced by the electron attachment to NMF and d_3 -NMF. Two peaks were observed: one with a maximum near 3 eV and a broader peak with a maximum near 9 eV. The anion signals for m/z 58 could be due to the loss of $\text{H}\cdot$ from the methyl group, the amide group, or the aldehyde group of the NMF molecule. However, the [Parent-H] $^-$ signal at m/z 61 from d_3 -NMF confirms site-selectivity for the formation of this ion and excludes H loss from the methyl group



Example anion signals induced by electron attachment to N-methylformamide and N-methyl- d_3 -formamide. The most abundant anions formed are CN^- and OCN^- . The resonances at m/z 61 show that cleavage from the methyl group does not occur, confirming site-selective dehydrogenation.

Our Reference: AP0821

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PAPER REFERENCE:

M. M. Dawley & S. Ptasinska (2014)
"Dissociative electron attachment to gas-phase N-methylformamide"
Int. J. Mass Spectrom. **365-366**, 143-151

HIDEN PRODUCT:

IDP

FUNDING:



U.S. DEPARTMENT OF
ENERGY

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Reactions of ethanol on Ru(0001)

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Recently constructed and optimized experimental high vacuum chamber for gas-phase DEA studies at NDRL with M. Michele Dawley, Sylwia Ptasíńska, and an undergraduate, Joanna Kabuye (from right to left).

of NMF. Peptide bond (O=C-N-H) cleavage was also observed resulting in both CH_3NH^- and HCO^- , minor dissociation channels requiring higher energies (> 5 eV). The experimentally observed resonances and proposed reaction channels were explained in terms of newly estimated thermodynamic thresholds for their formation. Our results showed that precise control of the impinging electron energy does affect the resulting fragmentation pathways induced by the DEA to NMF, especially regarding peptide bond cleavage. In addition, this study broadly contributes to understanding the ionizing radiation effects on amino acid, peptide, and protein structures. This investigation serves as a starting point for DEA studies of larger molecules, particularly longer chain molecules containing the peptide bond.

FIGURE 1 [RIGHT]: Set-up for studying surface reactions with TPD and RAIRS. This set-up is attached to an EUV source, such that photo-induced reactions can be studied as well.

FIGURE 2 [FAR RIGHT]: TPD spectrum of ethanol adsorbed on Ru(0001) below 100 K, showing the desorbing products ethanol, hydrogen and carbon monoxide.

Surface reactions on metallic surfaces are important for applications as catalysis, fuel cells and capping layers for optics in extreme ultraviolet (EUV) lithography tools. For all these applications, insight in the mechanisms of adsorption and reactions of molecules on surfaces is critical for fundamental understanding, as well as for further development of new materials and processes for applications. In this publication we investigate the reactions of ethanol on the (0001) crystal face of ruthenium with the aid of temperature-programmed desorption (TPD) and reflection-absorption infrared spectroscopy (RAIRS). This research was carried out in the EUV lab research group, located at ASML Research in Veldhoven, the Netherlands. This group is an integral part of the Industrial Focus Group XUV Optics from the MESA⁺ Institute for Nanotechnology, University of Twente, the Netherlands. Due to the high sensitivity of TPD carried out with a quadrupole mass spectrometer with secondary electron multiplier and pulse-counting electronics, sub-monolayer coverages of molecules can be readily detected.

Our results show that a part of the adsorbed ethanol molecules desorbs as intact ethanol, while another fraction undergoes abstraction of the CO group and H atoms, leading to desorption of molecular hydrogen and carbon monoxide, as well as deposition of surface carbon on the ruthenium. From the desorbing reaction products, in combination with RAIRS measurements, it could be derived that this reaction proceeds via an oxametallacycle intermediate, which has also been reported for several other metal surfaces. The surface carbon arising from the decomposition reaction poisons the Ru surface for next reactions cycles, which leads to gradual deactivation of the surface. Finally, the quantitative nature of TPD allowed us to make estimates about the amount of molecules that desorb molecularly versus the fraction that undergo decomposition.



Our Reference: AP0591

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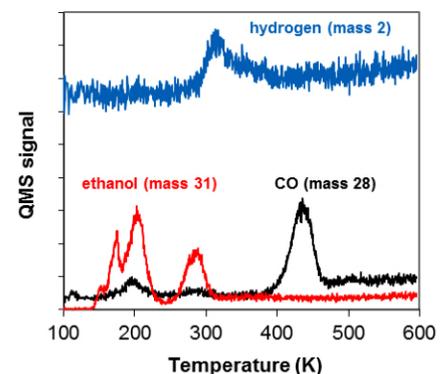
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PAPER REFERENCE:

J. M. Sturm, C. J. Lee & F. Bijkerk (2013)
"Reactions of ethanol on Ru(0001)"
Surface Science **612**, 42-47

HIDDEN PRODUCT:

3F PIC



Challenges and prospects for developing CdS/CdTe substrate solar cells on Mo foils

Thin-film CdTe solar cells boast lab-scale efficiencies above 20% when designed in the 'superstrate configuration' whereby the transparent front electrode is deposited first, on a glass superstrate. By inverting the design so that the front electrode is deposited last (i.e. the 'substrate' configuration), the cells can be fabricated on lightweight, flexible metal foils, thereby widening the range of possible applications. Here, ITO/CdS/CdTe/Mo solar cells have been grown in the substrate configuration by a combination of close-space sublimation and RF sputtering. A two stage CdCl₂ post-growth annealing process was developed, with the first stage contributing to CdTe doping and the second being linked to CdTe/CdS inter-diffusion. The inter-diffusion process was monitored using a Hiden Analytical secondary ion mass spectrometry (SIMS) system. Modelling of device performance predicts efficiencies as high as 11.3% may be obtainable upon formation of an Ohmic back-contact.

Substrate CdTe solar cells were processed as follows: on Mo foil substrates, *p*-type CdTe films (1.8 – 10 μm) were close space sublimation-deposited, from a powdered source. Then, by RF sputtering, *n*-type CdS window layers (200 nm) and the ITO front contact layers (200 nm) were deposited. Preliminary testing indicated that the standard CdCl₂ annealing process used for superstrate devices (typically a 20 min anneal of the CdS/CdTe stack at 420°C following CdCl₂ evaporation) was ineffective for substrate cell activation. Hence, in order to optimize the device processing, different CdCl₂ post-growth treatments were tested: Treatment A) a single air-anneal at 420°C following CdCl₂-deposition onto CdS/CdTe stacks; Treatment B) a single air-anneal following CdCl₂-deposition onto just the CdTe layer, but before CdS deposition; and Treatment C) identical to treatment B, but with a *second* air-anneal (480 – 580°C) introduced after ITO/CdS deposition.

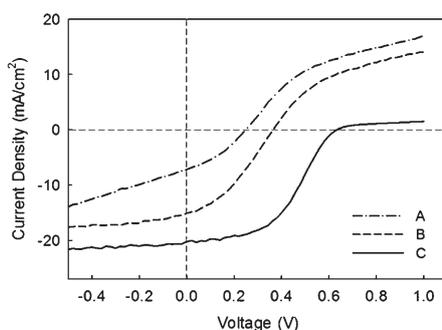


FIGURE 1: Current-voltage (*J-V*) curves of substrate configuration CdTe solar cells, obtained after applying different post-growth CdCl₂-treatments, A-C. *Modified from the paper reference.

Figure 1 shows the current-voltage (*J-V*) curves of the best performing ITO/CdS/CdTe/Mo devices obtained from each of the post-growth treatments. All devices subject to post-growth treatment A performed poorly, the majority of contacts were short-circuits while the remainder typically had $\eta < 0.5\%$. Devices subject to post-growth treatment B, also performed poorly, with the highest efficiency achieved being $\eta = 1.96\%$. Post-growth treatment C however (twice-annealed) yielded significant performance enhancements ($\eta \sim 5 - 6\%$), principally as a result of enhancements to V_{oc} and FF , implying an improvement in junction quality. A peak efficiency of 8.01% was finally achieved using treatment C upon

Our Reference: AP0811

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PAPER REFERENCE:

B.L. Williams, J.D. Major, L. Bowen,
L. Phillips, G. Zoppi, I. Forbes, K. Durose
(2014), "Challenges and prospects for
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cells on Mo foils" *Sol. Energy Mat. & Sol.
Cells*. doi:10.1016/j.solmat.2014.01.017

HIDEN PRODUCT:

IG20 gas ion gun in combination with a
quadrupole EQS 1000 analyser

incorporating a ZnO buffer layer between CdS and ITO (see Paper reference); this represents the best Cu-free substrate CdTe device reported. Whilst the first annealing stage, i.e. Cl-activation of the CdTe layer, is known to enhance *p*-type doping of CdTe, the impact of the second annealing stage on the composition of the stacks was investigated using SIMS profiling. Two devices were analysed, one having been annealed once (Treatment B, $\eta = 1.96\%$) and one having been annealed twice (Treatment C, $\eta = 6.05\%$). Figure 2a shows that S diffusion into the CdTe layer is enhanced by the second anneal: Inter-diffusion of S and Te is thought to assist in the passivation of surface defects at the interface and therefore lead to reduced

interface recombination. The improvements in V_{oc} and J_{sc} affected by the second annealing step are consistent with this. Figure 2b shows there is also a distinct difference in the Cl-profiles of the two devices: In the device subject to two annealing stages (C) there is a higher Cl concentration in the CdS layer and in the bulk of the CdTe, and this is likely to induce beneficial morphological changes in the junction region, i.e. recrystallization of both materials to minimise strain. It is evident that, for effective activation of substrate cell devices, a two-stage annealing process is necessary. This work is to be continued at the Stephenson Institute for Renewable Energy by Dr. Jon Major within the UK Photovoltaic Centre for Doctoral Training.

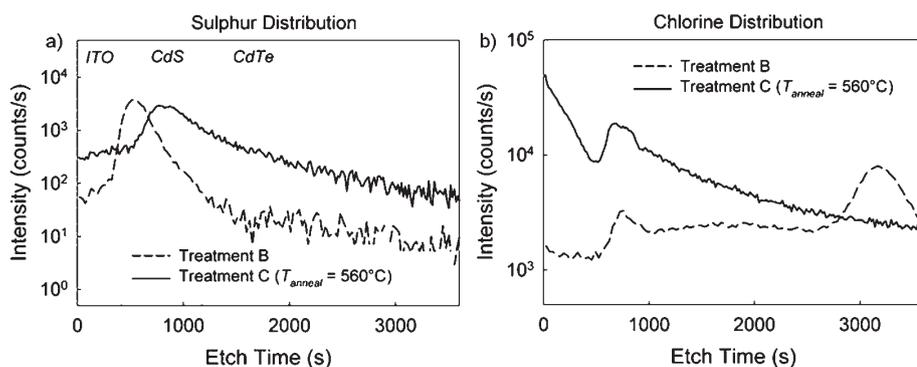


FIGURE 2: SIMS depth profiles of S^- and Cl^- in ITO/CdS/CdTe stacks that were subject to treatment B (single-anneal) and treatment C (double-anneal). The left edges of the plots represent the front surfaces of the cells, i.e. the ITO surfaces.

Chasing Stardust

The material density is remarkably variable in the space between the stars (the interstellar medium or ISM) with the densest regions consistent with good laboratory ultrahigh vacuum (UHV). Surprisingly, these dense regions are chemically the richest in space with more than 180 different types of molecules detected to date. However, detection of molecules does not tell us from where the molecules come or how important they might be! Astrochemistry addresses the first question while astrophysics tells us that certain small molecules, such as CO and H₂O, are crucial for the formation of long-lived stars like our Sun. They do so by cooling clumps of gas collapsing due to gravity, and on their way to becoming stars, by radiating their thermal energy away. Indeed that is how we know the molecules are there! Without these molecular coolants more massive, hotter and short-lived stars would emerge from the star formation process leaving little time for the chemical and biological evolution necessary for life on any suitable planets orbiting the stars.

However, the densest regions are the coldest at temperatures of 10-15 K, when many molecules including CO are found in solid form on interstellar dust grains. Desorption of CO must therefore happen for this molecule to be used as a coolant for star formation. Conducting temperature programmed desorption experiments allows us to investigate the sublimation of CO from models of these dust grains.

We have constructed, and use, a unique UHV system shown in Figure 1 below. This chamber is capable of conducting dynamic and static experiments and combines thermal atomic and molecular beam capabilities with surface analysis through infrared spectroscopy and thermal desorption mass spectrometry [1].



FIGURE 1: The Heriot-Watt University laboratory astrochemistry experimental ultrahigh vacuum chamber with the Hidden QMS outlined in red.

The CO desorption experiments were conducted by dosing 0.03 to 13.3 monolayers of CO on a Cu sample coated with 300 nm amorphous silica (SiO₂) cooled to 20 K. Heating the sample and measuring the gas-phase concentration of desorbed CO with a line-of-sight QMS (Hiden, HAL301) as a function of temperature yields kinetic information on the CO desorption.

CO ballistically deposits on a SiO₂ surface and exhibits first order desorption at coverages up to and including a monolayer (Figure 2 left panel). The peak temperature of desorption of CO decreases with increasing coverage as the monolayer is completed. Inversion analysis of the data, assuming a pre-exponential factor of 10¹² s⁻¹, tells us that as the coverage increases from 0.03 ML to 0.6 ML then the activation energy for desorption is reduced from as much as 12.2 kJ mol⁻¹ to 8.2 kJ mol⁻¹. The CO molecule is

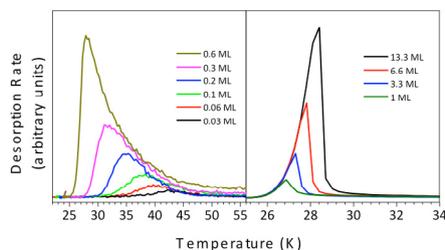


FIGURE 2: TPD spectra showing the impact of multiple binding sites on the sub-monolayer desorption of CO from SiO₂ (Left Panel) and how the temperature of desorption changes as the coverage is increased in the multilayer regime (Right Panel).

Our Reference:
AP-RGA-0008**PROJECT SUMMARY BY:**

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PAPER REFERENCE:

H. Fraser, W. Brown & M. McCoustra (2015) 'Chasing Stardust' *Chemistry World* August 2015. Print

HIDEN PRODUCT:

HAL 301

essentially probing a range of binding sites on the SiO₂ surface with increasing weaker binding strength as the coverage is increased.

Once the monolayer is completed, increasing the coverage further, 1 ML to 13.3 ML, brings us to a regime where the TPD data have aligned leading edges and the peak desorption rate moves to increasingly higher temperature. This is characteristic of zeroth order desorption of the multilayer. Arrhenius analysis of the data gives a pre-exponential factor of 10^{28±2} molecules cm⁻¹ s⁻¹ and a desorption energy for the CO film from SiO₂ of 7.3 ± 0.2 kJ mol⁻¹ [2].

Knowing the desorption kinetics of CO (and that of other molecules and mixtures of these molecules) from dust grain analogues allows us to understand the rate at which species are returned to the gas phase in the warmer star-forming regions of the ISM and hence their likely impact on the star formation process itself [3].

References :

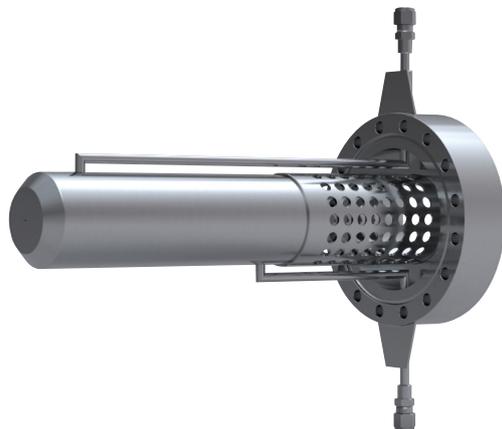
- [1] V. L. Frankland, A. Rosu-Finsen, J. Lasne, M. P. Collings, and M. R. S. McCoustra, *Rev. Sci. Inst.*, 2015, 86, 055103
- [2] M.P. Collings, V.L. Frankland, J. Lasne, D. Marchione, A. Rosu-Finsen, M.R.S. McCoustra, *Mon. Not. R. Astron. Soc.*, 2015, 449, 1826
- [3] M.P. Collings, M.A. Anderson, R. Chen, J.W. Dever, S. Viti, D.A. Williams, M.R.S. McCoustra, *Mon. Not. R. Astron. Soc.*, 2004, 354, 1133

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IDP - for analysis of ions, neutrals and radicals in UHV desorption studies

The Hidden IDP is for the direct analysis of low energy ions from UHV surface science techniques. Applications include electron stimulated desorption, photon stimulated desorption and thermal desorption studies:

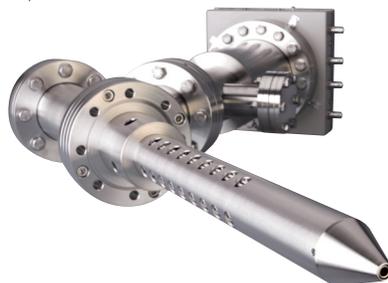
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Samples are loaded via a modular cassette sample holder and positioned using the computer driven high precision stage. Stored ion gun and analysis recipes will run the tool in fully automatic mode, reporting results in either spreadsheet or custom formats. The long life oxygen ion gun provides a stable beam for the full working day – and night, delivering surface spectra and 3D depth profiles. Analysis position and recipe can also be defined using a simple spreadsheet, allowing the non-expert user to complete a complex experimental matrix with ease.

Although the tool is designed to be run by nonspecialist technicians, the full range of SIMS parameters are available to more advanced users and the AutoSIMS can be used as a formidable research tool in its own right delivering unrivalled depth resolution and cost of ownership at this price.

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Hidden**APPLICATIONS**

Hidden's quadrupole mass spectrometer systems address a broad application range in:

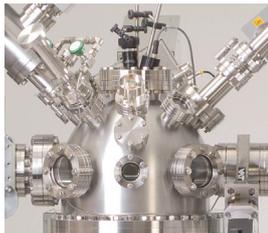
GAS ANALYSIS

- ▶ dynamic measurement of reaction gas streams
- ▶ catalysis and thermal analysis
- ▶ molecular beam studies
- ▶ dissolved species probes
- ▶ fermentation, environmental and ecological studies



SURFACE ANALYSIS

- ▶ UHV TPD
- ▶ SIMS
- ▶ end point detection in ion beam etch
- ▶ elemental imaging – 3D mapping



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