

## IV.I.23 Quantum Tuning of Chemical Reactivity for Storage and Generation of Hydrogen

H.H. Weiering (Primary Contact), M. Yoon,  
and Z.Y. Zhang

Oak Ridge National Laboratory

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### General Overview

This work is a joint experimental and theoretical study that focuses on establishing the fundamental underpinnings for chemical adsorption, dissociation, absorption, diffusion, and recombination of gaseous species on *quantum-mechanically confined thin films and alloys of light metal elements* with specific emphasis on hydrogen. Fundamental understanding of these quantum phenomena, including the quantum stabilization of thermodynamically immiscible alloy species and their potential for tuning surface catalytic processes, are directly relevant to the use of light-metal hydrides as storage media for hydrogen. Potential conceptual advances in this research area may also have a broader impact in gaining better understanding of the microscopic origin of catalysis, and in designing new types of catalysts for alternative energy and environmental applications.

During the first phase of the project, our experimental effort is primarily focused on growing atomically smooth ultrathin magnesium films on Mo(110) and Si(111) substrates and the investigation of quantum size effects on plasmon excitations and hydrogen adsorption. Theoretical efforts within first-principles approaches have been made in order to understand the fundamental properties of pure and alloyed Mg films and their interactions with hydrogen.

We have also carried out a combined experimental and theoretical study of the formation of surface alloys at the top of ultrathin metal layers of varying thicknesses grown in the quantum regime, and explored the corresponding changes in the surface activity as measured by the oxidation rates.

A parallel effort is undertaken to investigate the role of Friedel oscillations in the quantum stability of ultrathin films and the solubility of a second metal element, using Pb as a model system. Such *fundamental* understanding may lead to the creation of novel

metastable alloys with vastly improved properties for hydrogen storage or other applications such as plasmonics or superconductivity.

### Thin Film Growth

Low temperature growth of Mg on Mo(110) and Si(111) substrates results in the formation of atomically smooth thin films with precisely controlled film thickness, as indicated by scanning tunneling microscopy and Auger electron spectroscopy data. Depending on the growth temperature, Mg growth on Si(111) is preceded by the formation of an ultrathin silicide layer. On both substrates, Mg films grow in the hexagonal close packed (0001) orientation and the existence of discrete quantum well states was inferred from scanning tunneling spectroscopy data as a function of the film thickness.

On the theory side, we have investigated structural stabilities of  $Mg_{1-x}Al_x$  and  $Mg_{1-x}Na_x$  thin films and found that their formation energy as well as the Fermi energy and work function vary strongly with thickness. These effects seem to be closely related to quantum confinement effects. We have also carried out a more comprehensive model study of the quantum stability of metal films under various conditions and on different substrates, aimed to offer a critical assessment of the various factors contributing to the quantum stability.

### Quantized Plasmons

X-ray photoemission (XPS) experiments yielded compelling evidence for the importance of size quantization of the electronic properties, specifically the plasmons. Using XPS, we monitored the evolution of a sharp shake-up satellite in the Mg 1s core level as a function of the film thickness. For films with thicknesses between five and twenty five atomic layers the energy position of this peak is inversely proportional to the square of the film thickness. These results are consistent with the existence of *quantized* plasmons, which we interpret on the basis of theoretical (hydrodynamics and random-phase approximation) descriptions of the density-response function. We demonstrated that the observed loss feature corresponds to the  $n = 1$  *antisymmetric* (i.e., third) normal mode of the thin film, consistent with the fact that in the ultrathin film limit the symmetric plasmons have vanishing spectral weight—a striking manifestation of the role of size quantization on plasmon resonances in precisely controlled nanostructures.

The role of size quantization is also evident from the evolution of the plasmon loss intensity. We found that the plasmon creation probability after photoionization (i.e., extrinsic plasmon excitation) decreases with decreasing film thickness. This is qualitatively consistent with the notion that for a given quantum number (i.e.,  $n = 1$  *antisymmetric*), the perpendicular wave vector increases as the film thickness decreases, which in turn should lead to increased Landau damping of the volume plasmon and a reduction of the loss intensity. The observation of size quantization of plasmon modes adds an interesting new flavor to the concept of nanoplasmonics, including the possibility of tuning surface photochemical reactions via the plasmon resonance and its coupling to electromagnetic wave fields.

### Hydrogen Adsorption

We constructed a new system for temperature-programmed desorption (TPD) and succeeded in producing highly linear temperature ramps. Preliminary investigations of Mg desorption suggest rather complex line shapes for multilayer desorption, which are currently being analyzed. Atomically smooth Mg films with thicknesses ranging from 5 to 25 atomic layers have been exposed to atomic deuterium and their TPD spectra have been measured as a function of film thickness. The peak temperature for deuterium desorption varies from 463 K to 505 K, depending on the film thickness. We are currently exploring whether the variation can be attributed to quantum size effects. A complicating factor is the stability of the Mg film itself which desorbs at slightly higher temperature (539 K). The TPD data are currently being complemented with nuclear reaction analysis, scanning tunneling microscopy, and electron energy loss spectroscopy.

Theoretically, we find that the interaction of hydrogen with Mg thin films and thin film alloys is highly tunable. Structural properties such as the lattice spacing can be varied by several percents via alloying, whereas the work function can be tuned over a few tenths of an electron volt. The combined effects of alloying and lattice strain produce a very rich parameter space for tuning hydrogen binding energies. For example, we found that by applying strain of  $\pm 5\%$ , the work function changes by 0.6 eV and the H-binding strength changes by as much as 0.3 eV per hydrogen atom for a given film thickness. These fundamental findings open up new possibilities of using Mg films for realistic H-storage materials.

### Surface Alloying of Quantum Metal Films for Enhanced Chemical Reactivity

Using scanning tunneling microscopy and spectroscopy, we have demonstrated that the adsorption

of a minute amount of Cs on a Pb mesa grown in the quantum regime can induce dramatic morphological changes of the mesa, characterized by the appearance of populous monatomic-layer-high Pb islands on top of the mesa. The edges of the Pb islands are decorated with Cs adatoms, and the islands preferentially nucleate and grow on the quantum mechanically unstable regions of the mesa. Furthermore, first-principles calculations within density functional theory have shown that the Pb atoms forming the islands were expelled by the adsorbed Cs atoms via a kinetically accessible concerted place exchange process as the Cs atoms alloy into the top layer of the Pb mesa. These findings have important implications in quantum design of new types of catalysts via surface alloying, as illustrated by the greatly enhanced oxidation rates on the Cs-alloyed Pb films.

### Friedel Oscillations, Stability, and Kinetic Solubility

Because the quantum size effect is the key parameter for controlling the structure, morphology, and chemical reactivity of ultrathin metal film, we continue our line of research aimed at elucidating the origins of strong quantum size effects in Pb(111) which has been the model system of quantum-size-effect physics. Using first-principles density functional theory, we calculated the relaxations of the interlayer spacing in Pb(111) films. We find that both the sign and magnitude of the lattice relaxations oscillate with the distance  $x$  from the surface, and persist into the films with a  $1/x$  decay law. The interference of such persistent oscillations, in turn, can result in unusually large lattice relaxations at the center of the films, and the overall driving force is attributed to the Friedel oscillations in electron density, which also decays with a  $1/x$  power law. In contrast, for Pb(110), Pb(100), and Al(111) films, both the Friedel oscillations and interlayer relaxations decay with the standard  $1/x^2$  power law. One important conclusion is that the unusually slow decay of the Friedel oscillations in Pb(111) implies that the perturbation of the electron gas at one of the confining boundaries is felt by the other boundary of the film even if these boundaries are far apart, which explains why quantum size effects in Pb(111) films are so exceptionally robust. An intriguing question that remains to be answered is whether the  $1/x$  decay in Friedel oscillations could be attributed to Fermi surface nesting along the Pb [111] direction. This in turn would suggest that bulk alloys with nested Fermi surfaces would be good candidates for the exploration of quantum size effect physics.

A parallel experimental effort is aimed at tuning the thermodynamic solubility of metal alloys via the quantum size effect, using  $Pb_{1-x}Ga_x$  as a prototypical alloy system for showing exceptionally strong quantum size effects in the nanoscale regime and zero miscibility in the bulk limit. The underlying idea is that alloying provides an independent means of tuning the electronic

structure and surface chemical reactivity of quantum confined crystalline thin films. We find that atomically smooth ultrathin films of  $\text{Pb}_{1-x}\text{Ga}_x$  alloy ( $x=0.06$ ) can be stabilized on a  $\text{Si}(111)7\times 7$  substrate through the quantum size effect. The superconductive properties of these films clearly indicate that Pb and Ga do alloy in the ultrathin film regime. Quantum stabilized growth defects, consisting of deep holes extending to the film-substrate interface, act as pinning centers for vortices in the superconducting state. The present study highlights the possibility of growing new alloys beyond the solid solubility limit and controlling critical state properties in the quantum regime.

### List of Papers

1. **Quantized Plasmons in Ultrathin Magnesium Films**, M.M. Özer, A.G. Eguiluz, and H.H. Weitering, *Phys. Rev. Lett.*, submitted.
2. **“Particle in a Box” Experiments in the Laboratory: Quantum Size Effects on Growth, Superconductivity, and Plasmon Excitations of Ultra-Thin Metal Films**, M.M. Özer, and H.H. Weitering, *J. Low Temp. Phys.*, submitted.
3. **Persistent oscillations in the interlayer lattice relaxation of Pb(111) films**, Y. Jia, B. Wu, T.L. Einstein, H.H. Weitering, and Z.Y. Zhang, *Phys. Rev. Lett.*, submitted.
4. **Magnetic doping of group IV semiconductors**, M.M. Özer, C.G. Zeng and H.H. Weitering, Invited Book Chapter in “Spintronic Semiconductors”, edited by Weimin M. Chen and Irina Buyanovaw, Pan Stanford Publishing, 2009 (in print).

5. **Surface Alloying and Morphological Restructuring of Quantum Metal Films for Enhanced Chemical Reactivity**, Alexander Khajetoorians, Wenguang Zhu, Jisun Kim, Shengyong Qin, Holger Eisele, Zhenyu Zhang, and Chih-Kang Shih, *Proc. National Academy of Sci.* submitted.
6. **Interaction between Dihydrogen and Metallofullerenes**, M. Yoon, S. Yang, and Z.Y. Zhang, *J. Chem. Phys.*, submitted.
7. **Stability of metallic thin film with free electron model**, B. Wu and Z.Y. Zhang, *Phys. Rev. B* 77, 035410 (2008).
8. **Calcium as the Superior Coating Metal in Functionalization of Carbon Fullerenes for High-Capacity Hydrogen Storage**, M. Yoon, S.Y. Yang, C. Hicke, E.G. Wang, D. Geohegan, and Z.Y. Zhang, *Phys. Rev. Lett.* 100, 206806 (2008).

### Personnel

- H.H. Weitering,  
Research Staff and Joint Faculty Member (30%)
- Zhang,  
Research Staff and Joint Faculty Member (15%)
- Yoon  
Research Staff Member (33%)
- M.M. zer  
Postdoctoral Rese-archer (100%)