Quantum size effect induced modification of the chemisorption properties of thin metal films

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We present temperature programmed desorption data and inverse photoemission (IPE) spectra that directly demonstrate the effects of quantum confinement of electrons in an ultrathin metal film on molecular chemisorption at the film's surface. The prototypical system of CO adsorbed on the *n*-monolayers-Cu/fccFe/Cu(100) [$2 \le n \le 15$] was explored. For all films, the CO peak desorption temperature (T_{des}) is lower than that of Cu(100). Moreover, oscillations in T_{des} are correlated with oscillations in the IPE intensity at the Fermi level (E_F) caused by metallic quantum well states in the Cu overlayer passing through E_F as function of film thickness.

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When the thickness of a metal film reaches nanometer length scales, the valence level wave functions become confined in the direction perpendicular to the plane of the film. As a result, the electron energy spectrum of the system acquires discrete features. These so-called metallic quantum well (MQW) states have been associated with a wide range of new and interesting physical properties of nanoscale metal films including the oscillatory magnetic exchange coupling that gives rise to the giant magneto-resistance effect in magnetic multilayers,^{1–5} magic layer numbers in thin film growth,^{6–8} oscillatory interlayer relaxations in metal islands,^{9,10} thickness-dependent conductance anomalies¹¹ and work function modulations.¹² Theoretical calculations have predicted that the interaction between a planar metal surface and atoms or molecules can be modified by quantum size effects (QSEs),¹³ however such effects have not been observed experimentally. Tailoring chemisorption properties is a long-standing goal of surface science and accomplishing this through QSEs represents an entirely new approach to the problem. Typically, chemical modification is achieved by deposition of a monolayer or submonolayer overlayer of a second metal, through surface alloy formation,¹⁴⁻¹⁸ or by forming nanoscale metal dots on a semiconductor substrate.¹⁹ These methods change the behavior of the surface atoms through a local mechanism such as charge exchange or site blocking. The impact of QSEs on chemistry has been observed in the gas phase, however, where metal clusters with "magic numbers" of atoms associated with closed electronic shells exhibit unusually high or low chemical reactivity.^{20,21} As modern applications demand metal films that are increasingly thin, electronic QSEs in films could play an important role in processes such as molecular selfassembly, atomic layer deposition, friction in NEMS devices, and surface photochemistry.

In this paper we provide experimental evidence that the interaction between atoms or molecules and metal surfaces may be manipulated by employing the electronic QSEs exhibited by two-dimensional metal nanostructures. Moreover, as the electronic properties of these nanostructures can be varied while their surface geometric structure is essentially unchanged, one can distinguish between structural and electronic effects in the molecule-surface interaction. We report on the adsorption properties of the prototypical diatomic molecule CO on nanometer-scale-thick Cu(100) films and we have found that the energy of adsorption exhibits systematic changes as a function of Cu thickness. In addition, these changes are directly correlated to the behavior of the MQW states in the Cu film. For all films that we investigated, the CO peak desorption temperature, T_{des} , of the temperature programmed desorption (TPD) spectrum is reduced from that of CO on the single crystal Cu(100) surface. Most interestingly, we find that T_{des} oscillates as a function Cu overlayer thickness. T_{des} has a local maximum at Cu thicknesses where a MQW state crosses the Fermi level, $E_{\rm F}$, and is reduced for thicknesses in between. These results show a direct influence of QSEs on chemisorption and indicate that the metal *sp*-electrons are responsible for the effects we observe.

The experiments were performed in a single ultrahigh vacuum chamber that contains thermal evaporation sources for metallic thin film deposition, isochromat inverse photoemission (IPE) spectroscopy, TPD, and a wide array of surface characterization techniques including low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). Initially, a Cu(100) surface was prepared by standard polishing and sputter-anneal cycles after which 5 monolayers (ML) of Fe were deposited by physical vapor deposition at room temperature. The Fe film grows layer-by-layer²² in a fcc structure²³ and forms a closely lattice-matched template for a Cu overlayer, which also grows layer-by-layer²² from 2 to 15 ML thickness. This Cu overlayer forms the MOW in which the electrons are confined. Upon MQW formation, IPE measurements were performed to verify that the film supports strong MQW states. The sample was then cooled down to approximately 100 K and dosed with CO until a sharp $c(2 \times 2)$ structure was observed in LEED; the compressed $(7\sqrt{2} \times \sqrt{2})$ structure found for higher CO coverages was carefully avoided. To examine the unoccupied states of the CO/MQW system, IPE spectra were acquired at normal incidence from the $c(2 \times 2)$ surface. Following this step, the sample was placed in front of the mass spectrometer and a TPD spectrum was obtained by monitoring the mass 28 signal while ramping the sample temperature at a constant rate of 1 K/s to a maximum of 300 K. After the TPD run, AES showed no traces of carbon or oxygen, indicating that CO desorbed molecularly. IPE and LEED measurements pro-



FIG. 1. IPE spectra obtained at normal incidence for the as-deposited (a) and CO covered (b) *n*-ML-Cu/fccFe/Cu(100) MQW system. In (a) individual MQW states increase in energy as a function of increasing Cu MQW thickness with the v=1 and v=2 crossing E_F at Cu thicknesses of ~5 and ~10 ML, respectively. These crossings modulate $I(E_F)$ substantially. MQW state features persist in the CO covered MQWs (b) and behave similarly to the MQW states in the as-deposited systems.

vided further evidence that the surface was clean and well ordered after desorption. We then deposited an additional monolayer of Cu, and the experiments were repeated. In this way, we have obtained measurements for MQWs of both the bare and CO covered system for a series of Cu thicknesses. We checked our results periodically by depositing a Cu MQW of a desired thickness in a single evaporation and then performing the CO exposure, IPE and TPD measurements. In all cases we obtained the same results as those given by our sequential depositions.

Figure 1(a) shows IPE spectra obtained at normal incidence from the Cu/fccFe/Cu(100) system for a series of Cu overlayer thicknesses. The spectra exhibit well-defined features, labeled by the quantum number v,^{4,24} which shift to higher energy with increasing Cu MOW thickness. These features are Cu MQW states and their thickness dispersion saturates at $\sim 2 \text{ eV}$ above the $E_{\rm F}$, which is the X'_4 -point of the Cu band structure along the (100) direction. Periodically, a MQW state passes through $E_{\rm F}$, causing the IPE intensity at the Fermi level $[I(E_{\rm F})]$ to modulate substantially. A closer inspection of Fig. 1(a) shows that $I(E_{\rm F})$ exhibits a maximum at d=5 ML as the v=1 MQW state crosses $E_{\rm F}$, then reduces for greater thicknesses until near d=10 ML where the v=2MQW state becomes unoccupied. These results are essentially identical to IPE measurements in the literature obtained using a grating spectrograph.^{3,4}

Figure 1(b) shows normal incidence IPE spectra obtained from 0.5 ML CO adsorbed on the Cu/fccFe/Cu(100) system for a series of Cu MQW thicknesses. The broad feature peaked near 3.75 eV is associated with the CO $2\pi^*$ antibonding level, and a comparison to the equivalent feature for $CO/Cu(100)^{25}$ is discussed elsewhere.²⁶ Of primary concern to us is the behavior of these spectra near $E_{\rm F}$. We observe spectral features that change systematically with Cu overlayer thickness in a way that is very similar to what is seen for the bare MQW system. For the lowest two Cu coverages, there is a local maximum in the emission that occurs near 1.75 eV above $E_{\rm F}$. At 5 ML Cu thickness, a feature appears at $E_{\rm F}$ and $I(E_{\rm F})$ rises accordingly, whereas for larger Cu thicknesses, the same feature moves to higher energy and $I(E_{\rm F})$ decreases. At a Cu thickness of 10 ML, a second feature crosses the $E_{\rm F}$, and $I(E_{\rm F})$ is enhanced again. This feature moves to higher energy for the largest two thickness and $I(E_{\rm F})$ decreases again. Although the peaks are less intense and slightly modified by the presence of the adsorbate, these data show that the Cu MQW states still exist in the COcovered system

To investigate how MQW states affect the chemisorption of small molecules, TPD measurements of the CO/Cu/fccFe/Cu(100) system were performed. Increases or decreases in the strength of bonding of the CO to the Cu



FIG. 2. CO-TPD spectra for a series of Cu MQW thicknesses. The T_{des} oscillates as a function of Cu thickness exhibiting maxima at 5 ML Cu thickness and 10 ML Cu thickness. The peak desorption temperatures for the MQWs are lower than the value for bulk Cu(100) but approach the bulk value as the Cu thickness increases.

MQW will, respectively, raise or lower the T_{des} . Furthermore, changes in the desorption pathway, i.e., deviations from firstorder behavior, will be evident in the line shape of the TPD spectrum. Figure 2 shows a series of TPD curves obtained from the CO/Cu/fccFe/Cu(100) system for different Cu MOW thicknesses. The upper curve is from CO adsorbed directly on the single crystal Cu(100) surface. Comparing the TPD spectra of CO from the MQW systems we find that their line shapes are very similar to that of CO from the single crystal Cu(100) surface indicating that the desorption process remains first order. A second observation is that T_{des} is lower for all of the MQW systems than it is for Cu(100), which strongly suggests that the peaks represent desorption from the terraces of the films, rather than from defects or film imperfections (note, the weak feature near 215 K in the TPD spectra is associated with desorption from step edges, and carries spectral weight similar to that found for the Cu(100)surface). Most important, however, we find that T_{des} is not the same for all MQW thicknesses, nor does it increase monotonically to the Cu(100) value, but instead oscillates as a function of Cu MQW thickness. The vertical dashed line in Fig. 2 indicates the centroid of the TPD peak from the 2 ML Cu film and shows clearly that this peak is centered about 10 K below that of Cu(100). The spectra of Fig. 2 show that T_{des} increases with thickness up to a maximum at 5 ML, then decreases to a minimum at 7.5 ML Cu thickness after which it begins to increase again. For thicker films, T_{des} reaches a second local maximum near 10 ML and then shows a small reduction for the two greatest thicknesses. The shifts in T_{des} for the thicker films are small but highly reproducible.

To examine the relationship between the chemisorption properties of CO and the MQW states of these Cu overlayers, we plot in Fig. 3 both $I(E_{\rm F})$ and $T_{\rm des}$ as a function of Cu thickness. As is obvious from these curves, these two quantities are highly correlated. Both curves exhibit a local maximum at $\theta_{\rm Cu}$ =5 ML followed by a minimum near 7.5 ML and then a gradual increase to a second maximum near 10 ML followed by a subsequent decline. Note that for both quantities, the overall trend with increasing Cu thickness is toward the values observed for the single crystal Cu(100) surface.

As mentioned previously, changes in desorption temperature have been seen for a number of bimetallic systems,¹⁷ but those cases have been restricted either to films in the subor few-monolayer range, or to alloy formation. In those cases, the modification to chemisorption could be understood as either a local change in electronic structure (i.e., charge transfer) or as a substitutional effect where an inert member of a binary alloy trades off with an active member as a function of alloy composition. As we have grown all films at or below room temperature, our systems show no indication of alloy formation for Cu MQWs that are 2 ML or thicker. The overall reduction in T_{des} may be the result of the interaction between the less-reactive Cu overlayer and the more reactive Fe film, similar to what has been found for Pd/Ru(0001).^{17,18} Such behavior is often linked to shifts in the centroid of the d-band. Recent first principles calculations show that a d-band shift toward $E_{\rm F}$ for up to 3 ML of Pd on the noble metal Au is accompanied by an increase in Pd reactivity.²⁷ These effects recover rapidly (within $\sim 1-2$ ML) and monotonically to the single crystal surface value. Normal emission photoelectron spectra²⁸ from Cu/fccCo/Cu(100) do reveal changes in the Cu d-levels as a function of MQW thickness. However, the centroid moves slightly *away* from $E_{\rm F}$ with increasing thickness suggesting monotonically weaker CO bonding. It is possible that, when integrated over the entire d-band, the centroid moves toward $E_{\rm F}$ for thicker films. Either way it is undoubtedly true that the Cu d-levels play an important role in the bonding, but it is unlikely that changes in the *d*-levels are responsible for oscillations in T_{des} in this system. As the QSEs persist in films that are 10 ML or more in thickness, the T_{des} oscillations do not appear to be associated with charge transfer at the Fe-Cu interface. The correlation between the $I(E_{\rm F})$ and $T_{\rm des}$ strongly suggests that MQW states are responsible for the oscillatory changes in $T_{\rm des}$ that we observe and, more specifically, changes in the Cu electronic levels at or near $E_{\rm F}$ dominate the effect. As MQW states pass through $E_{\rm F}$, that part of the moleculesurface interaction mediated by the Cu sp-levels is modified. The MQW states are essentially two-dimensional and thus



FIG. 3. Plot of T_{des} [open circles] and $I(E_F)$ [closed squares] as a function of Cu thickness. There is a strong correlation between the two quantities indicating that QSE modify the chemisorption of CO to Cu MQWs.

there is a step-like change in the density of states (DOS) at the bottom of a subband. The maxima in $I(E_{\rm F})$ at $k_{\parallel}=0$ therefore correspond to sub-bands crossing the $E_{\rm F}$ and enhancing the DOS at $E_{\rm F}$ available for the CO-Cu bond as observed by the two $T_{\rm des}$ maxima at 5 ML Cu and 10 ML Cu. As these MQW states are predominantly of *sp*-character, our results provide direct evidence for the role of *sp*-electrons in the CO-metal bond in this system. Between these $E_{\rm F}$ crossings, $T_{\rm des}$ falls as $I(E_{\rm F})$ falls, suggesting that not the all of the electrons in the *sp*-subband are involved to the same extent in the bonding.

The usual starting point for a description of the COtransition metal bond is the Blyholder model²⁹ where bonding is viewed as proceeding by donation of charge from the highest occupied molecular orbital, which in this case is the CO 5 σ orbital, to the metal *d*-levels, followed by backdonation from the *d*-levels into the lowest unoccupied molecular orbital, in this case the CO $2\pi^*$. In this model, the origin of a correlation between $I(E_{\rm F})$ and $T_{\rm des}$ is not obvious as the Cu states at $E_{\rm F}$ are primarily of *sp*-character. However, in further theoretical investigations, specifically designed to address the interactions of CO with Cu (which has filled d-bands), Gumhalter and co-workers³⁰ emphasized the involvement of the Cu sp-levels, particularly in the backdonation part of the interaction. Along similar lines, in cluster calculations modeling CO adsorption on Cu(100), Bagus and co-workers³¹ found indications that the interaction with the sp-electrons may in fact dominate metal-adsorbate bonding in this system. Modification of this portion of the COmetal bond by QSEs would explain the observed correlation between $I(E_{\rm F})$ and $T_{\rm des}$. Norskov and co-workers³² found a correlation between the energy location of the centroid of the transition metal *d*-band and the strength of adsorption as measured by the CO thermal desorption temperature. In this treatment, interactions with the *d*-electrons appear to dominate the bonding when the *d*-band is partially occupied. The location of the centroid of the Cu *d*-levels may play a role in the initial reduction of T_{des} and its subsequent trend toward the Cu(100) value, but it does not explain the observed oscillations in T_{des} . On the experimental side, recent x-ray emission spectroscopy studies of the CO/Cu(100) system give direct evidence for the participation of Cu *sp*-electrons in the chemisorption bond.³³ Theoretical efforts to identify the exact nature of the interactions in this system are in progress.³⁴

The results described here suggest using MQWs in nanoscale metal systems as a new way to engineer moleculesurface interactions. Aside from bonding strength, many other properties, such as vibrational energies, bonding sites, the competition between molecular desorption and dissociation, and surface photochemical processes may be tailored when molecules are adsorbed on MQWs. In one- and zerodimensional nanostructures, where QSEs induce stronger modulations in the DOS, these effects should be even more pronounced. Such control of molecule-metal adsorption properties may prove particularly interesting in the case of thiols and related organics owing to their prevalence in the emerging field of molecular electronics.

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