The study of metal surface and metal thin film

Atomic structure

Electronic structure

Cr(100)

Be(1010)
Energy range of the electrons sensitive to the surface
Use electrons as source to study surface and thin film

Electrons work as waves

Imaging
Diffraction
Interference contrast

Low Energy Electron Microscopy
Low Energy Electron Microscopy (LEEM)
Phase contrast

• Atomic step contrast

Step edge

Energy → wave length
Providing atomic resolution information perpendicular to the surface.
Phase contrast

- **Quantum size contrast**

  Thin film

  Energy $\rightarrow$ wave length

  Providing atomic resolution information perpendicular to the surface.
Lattice structure of Cr(100)

Real space

Diffraction pattern by LEEM
Surface morphology

Coarsening and Oswald ripening effect (T= 936 K~ 1070K)

Different mechanism for the expansion of the vacancy island
(T=1079 K ~ 1097 K) → Vapor pressure ~ 10^{-8} Torr
Surface morphology

T = 1186 K

A, A’ Expanding vacancy island

B Single spiral

C 3D mound of adatom islands
The core hole of a spiral is the Screw dislocation terminating at the surface
The motion of double spiral

- $T = 1113$ K
- $T = 1136$ K
- $T = 1146$ K
- $T = 1166$ K
Strategies

What we can do by LEEM is to measure the
1. Time dependence of the step edges
2. Temperature dependence of the step edges
And then compare them with the results of theoretc model
BCF model for surface sublimation

Expanding vacancy island

Detached from step edge

Surface diffusion

Desorption

$r = R$ ← Increasing over time → $r = 0$
Linear time dependence $\Rightarrow$ Vacancy island radius

The adatom concentration $c(r,t)$

$$D\nabla^2 C(r,t) - \frac{C(r,t)}{\tau} = \frac{\partial}{\partial t} C(r,t)$$

$C(r) = A I_0 \left( \frac{r}{\sqrt{D\tau}} \right)$

$C(R) = C_\infty \exp \left( -\frac{\gamma \Omega}{R k_B T} \right) \approx C_\infty$

$$\frac{dR}{dt} = D \Omega |\nabla C(r)|_{r=R} = \sqrt{\frac{D}{\tau}} \Omega C_\infty \frac{I_1 \left( \frac{R}{\sqrt{D\tau}} \right)}{I_0 \left( \frac{R}{\sqrt{D\tau}} \right)}$$

Vacancy island radius $R(t)$

$$R(t) = \sqrt{\frac{D}{\tau}} \Omega C_\infty t - O(\ln(t))$$
Temperature dependence ⇒ Activation energy

Step velocity

\[
\frac{dR}{dt} = \sqrt{\frac{D}{\tau}} C_\infty \propto \exp\left(-\frac{2E_f + E_d + E_a}{2k_B T}\right)
\]

\[E_f + (E_d + E_a)/2 = 3.0 \pm 0.2 \text{ eV (V island)} \]
\[3.3 \pm 0.1 \text{ eV (D spiral)}\]

Rotation frequency (sublimating rate)

\[\omega = \omega_0 \exp\left[-\frac{(E_f + E_a)}{(k_B T)}\right]\]

\[E_f + E_a = 3.6 \pm 0.2 \text{ eV.}\]

The enthalpy of sublimation of Cr, 3.7 eV
Ag/Cr(100)

1 HOUR LATER

445 C

467 C
7.5 eV  Ag/Cr(100)  16.7 eV

38.5 eV  51.5 eV
I V curve

\[ \Phi = 2kt = \left(\frac{2t}{\hbar}\right)\sqrt{2m(E + V_0)} \]
Film growth on the step edges
Use photons as source to study surface and thin film

Photons work as particles

Kicking electrons out

Photoemission
Photoemission

Excited electron and hole states

Photoemission

Excited electron state (photoelectron)

Excited hole state (Initial)

Conduction band

Valence band

Work function

Photon

Initial

\( \omega \eta = -\Phi - E_b \)

\( E_f - E_i = \eta \omega \)

\( E_k = \eta \omega - e\Phi - E_b \)

\( E_b = -E_i \)
Photoemission

\[
\begin{align*}
\hat{n}\omega & = \sqrt{\frac{2m}{\hbar^2}} \sqrt{\hbar\omega - \varepsilon_B - \phi \sin \theta} = \sqrt{\frac{2m}{\hbar^2}} \varepsilon_{\text{kin}} \sin \theta \\
E_k &= h\omega + E_i - e\phi
\end{align*}
\]
After passing through the lens set, electrons with energies equal to $E_{\text{pass}}$ within uncertainties $\Delta E$ will travel around the equipotential $V_0$ surface and reach the exit slit.

\[ E_{\text{pass}} = e(V_1 - V_2)(\frac{R_1 R_2}{R_2^2 - R_1^2}) \]

\[ \frac{\Delta E}{E_0} = \frac{w}{2R_0} + \beta^2 \]
2D band mapping

- 3rd generation Imaging-Type analyzer
- Spatial mapping
- Angular mapping

State of the art:
- $\delta E = 10$ meV
- $\delta A = 0.1$ degrees
Photoemission end station in SRC
Photoemission end station in CAMD
Surface state and Quantum well state
Strategies

What we can do by the Photoemission is to measure

1. Band dispersions
2. Photon energy dependence
3. Temperature dependence
4. Thickness dependence

And then compare them with the results of theoretic model
Quantum well states

Bohr-Sommerfeld quantization rule

\[ k_\perp = \frac{2n\pi - \phi_s(E) - \phi_i(E)}{2Nt} \]

\[ E_n = E(k_\perp) \]

n: Quantum number, 1,2,3,..
Nt: thickness
\( \phi \): interface phase shift
All the information of substrate bands are embedded in \( \phi_i \)
Quantum size effect

Ag qws bands parallel to the surface, which are normally similar to the corresponding bulk band dispersions.
Atomically uniform film revealed by photoemission

1 ML

qws peak

1 ML

1.5 ML

1 ML 2 ML
Atomically uniform + quantum size effect

Thickness changes (uniform films)

- The allowed quantized $k_\perp$'s changes
- The energy positions of the QWS changes
- Properties of films change

Surface energy, work function, thermal stability, adsorption, superconductivity transition temperature, magnetic interlayer coupling……….

Substrate effect

Thin film

Substrate
My three major findings on substrate effect

1. Many body interaction between the quantum well state and substrate state
   
   → Kink dispersion


2. Strong hybridization between the surface state and substrate bands
   
   → Display of HH,LH and SO major substrate bands


3. Diffraction from the substrate surface
   
   → QWS of second kind

Surface Brillouin zone for Ag(111) and Ge(111)
The band structures of atomically uniform thin film of Ag/Ge(111)

\[ \Gamma \rightarrow M \]
Band dispersions of Ag/Ge(111)

Two types of splitting !!

Type 1

Kink
Dramatic linewidth change of QWS across substrate band edge

Type 2

Layer resolution
The band structures of QWS in 8.6 ML are equal to the linear combination of 8ML and 9ML.
Atomically uniform film
Ag/Ge(111)
Atomically Uniform Film

Quantum well peak

1. moving discretely from its 8 ML (9 ML) position to the 9 ML (10 ML) position.

2. The 8ML (9ML) peak is absent in the 9ML (10ML) spectrum and vice versa.
Non quasiparticle behavior

The two-peak line shape across the substrate band edge is non quasiparticle

Retarded Green function for a single electron state entering into the bulk band continuum.

\[
G(E)^{-1} = E - E_q + i\delta_q - \int_{-\infty}^{E_0} \frac{|V|^2}{E - \varepsilon + i\delta_s} g(\varepsilon) d\varepsilon
\]

\[
g(\varepsilon) = \frac{A}{\sqrt{E_0 - \varepsilon}} \Theta(E_0 - \varepsilon)
\]

One dimensional form of the density of the states for the substrate band edge

Spectral function

\[
\rho(E) = -\frac{1}{\pi} \text{Im}(G) = -\frac{1}{\pi} \text{Im}\left(\frac{1}{E - E_q + i\delta_q - \pi|V|^2(E - E_0 + i\delta_s)^{-1/2}}\right)
\]
Surface state

$2\text{D electron state residing on or near the surface}$

$\text{The product of reduced symmetry}$

$$k_\perp = p + iq$$

$$\psi(z) \propto e^{-qz} \cos(pz + \delta)$$

When $1/q \geq Nt$

Surface state touches down to the substrate

Something interesting happens !!!
The anomalous lineshape of the surface state at lower thickness

Ag/Ge(111), Normal emission

Quantum well state? Substrate state?
Thickness dependence of the surface state dispersion

Decay length of Ag surface state \( \approx 12 \text{ML} \)

Surface state energy shifts with the thickness

\[
\Delta E(t) = \langle \varphi | \Delta V | \varphi \rangle = \Delta E(0) \exp(-2\beta t)
\]

\( \beta \approx 11.7 \)


New finding !!!
Thickness dependence of the surface state dispersion

Strong hybridization between the surface state and substrate states makes the photoemission intensity proportional to the density of states for substrate bands

\[ I(E) \propto |\langle \psi_s(E) | \psi(E) \rangle|^2 g(E) = |M|^2 g(E) \]

\[ g(E) = \sum_{i=1}^{3} \frac{A_i}{\sqrt{E_i - E} \Theta(E_i - E)} \]

Three major Ge bands of HH, LH and SO cross this area
Fitting the data with the model
Comparison with the calculated Ge bands and other measurements

Spin-orbital Splitting

Expt 0.301 eV
Optical measurements 0.296 eV

Effective Mass

Expt
HH 0.30
LH 0.034
SO 0.21
Cyclotron measurements
0.33 0.043 0.095
Quantum well state of the second kind
Ag bulk bands projected to (111) direction
Surface Brillouin zone for Ag(111) and Ge(111)
The Ge substrate working as a diffraction grating

\[
\mathcal{P}_{\bar{M}} = \mathcal{K}_{\bar{M}} - \mathcal{G}_{\parallel} \quad \mathcal{G}_{\parallel} = 2\mathcal{K}_{\bar{M}}
\]
Generalized Bohr-Sommerfeld quantization rule

\[ (k_{1\perp} + k_{2\perp} + k_{3\perp} + k_{4\perp})^* d + \phi = 2\pi n, \quad n = 1, 2, 3, 4 \]

\[ (k_{1\perp}(E_1) + k_{2\perp}(E_2) + k_{3\perp}(E_3) + k_{4\perp}(E_4))^* d + \phi = 2\pi n \]

Due to energy conservation

\[ (k_{1\perp}(E) + k_{2\perp}(E) + k_{3\perp}(E) + k_{4\perp}(E))^* d + \phi = 2\pi n \]

\[ K_{\perp}^{NEW} (E)^* d + \phi = 2\pi n \]

, \( d = N_t \), \( t = 2.36 \, \text{Å} \) for 1ML of Ag in (111) direction
Substrate is the key
Hybridization between qws of the first kind and qws of the second kind
Thickness dependence of hybridization between two different kinds of quantum well states

bands and bands anti-cross interactions

\[ \hat{H} = \begin{bmatrix}
E_1 & 0 & 0 & 0 & 0 & V & V & V & V \\
0 & E_2 & 0 & 0 & 0 & V & V & V & V \\
0 & 0 & E_3 & 0 & 0 & V & V & V & V \\
0 & 0 & 0 & E_4 & 0 & V & V & V & V \\
0 & 0 & 0 & 0 & E_5 & V & V & V & V \\
V & V & V & V & V & E_1' & 0 & 0 & 0 \\
V & V & V & V & V & 0 & E_2' & 0 & 0 \\
V & V & V & V & V & 0 & 0 & E_3' & 0 \\
V & V & V & V & V & 0 & 0 & 0 & E_4'
\end{bmatrix} \]

\[ V \ (\text{thickness}) = ? \]
Relationship between quantum well state and surface state from 5 ML down to 1 ML
Second kind of quantum well from 5ML down 1ML
Doping effect on the quantum well states

Atomically uniform film + quantum size effect + substrate effect

bulk
High Tc
Magnetism

film

Substrate
Surface Superconductivity on Be(10\bar{1}0)

\[ \lambda = \frac{N(0)\langle I^2 \rangle}{M\langle \omega^2 \rangle} \]

\[ k_B T_c = (\eta \omega_D / 1.45) \exp \left[ -\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right] \]

Bulk Be \hspace{1cm} \lambda = 0.24 \hspace{1cm} T_c = 0.024 \text{ K} 

Be(10\bar{1}0) \hspace{1cm} \lambda = 0.646 \hspace{1cm} T_c = 17 \text{ K} \rightarrow \text{Localized S1 state} \hspace{1cm} \text{Small coherence length } \xi 

\[ \xi = \eta \nu_F /(2\pi k_B T_C) \]

HTSC \rightarrow \text{Dominant e-p coupling with 50-80 meV optical phonon}

MgB_2

1. Light atoms
2. Covalent like sp B-B bonding with DOS at Fermi level
3. Dominant coupling with in-plane B-B vibration phonon about 64 meV
Back bonding model → rehybridization of broken surface bonds

Hybridization between S2 and SR states

Charge density distribution of SR and S2 on (0010) cut plane  

(J-H Cho)
Inversion symmetry