Quantum Size Effects in Thin Film Stabilities and Properties

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Abstract

Recently, it has been shown that the size quantization of itinerant electrons in an ultra thin metal film plays an important role in the early formation stages and kinetic stabiliy of thin films. This Quantum Size Effect(QSE) also brings about a lot of new interesting physical and chemical properties of thin film. In this paper, I will give a brief introduction to the mechanism of QSE and talk about some practical research examples to the thin film stabilities and properties.

1 Classical film growth modes

From a classical point of view, the formation and growth of a thin film is determined by both thermodynamic factors, such as the Gibbs free energy and kinetic factors, such as surface diffusion and deposition rate. In the thermodynamic limit, where the deposited species have enough thermal energy to diffuse and reach energy minimum distribution, the Gibbs free energy plays a key role to determine the morphology of thin film. Or, more precisely speaking, the change of Gibbs free energy in the growth process

$$\Delta G = V \cdot \Delta G_V + \Delta(A_S \cdot \gamma)$$

determines the final morphology. Here, V is the volume of thin film and A_S is the total surface of the thin film including the interfacial area. ΔG_V is the free energy per unit volume of thin film, γ is the surface energy density and $\Delta(A_S \cdot \gamma)$ is the corresponding surface energy change before and after deposition. If we only consider film with certain volume like Figure 1 below,

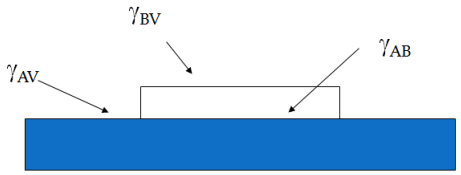


Figure 1: Thin film B deposited on substrate A

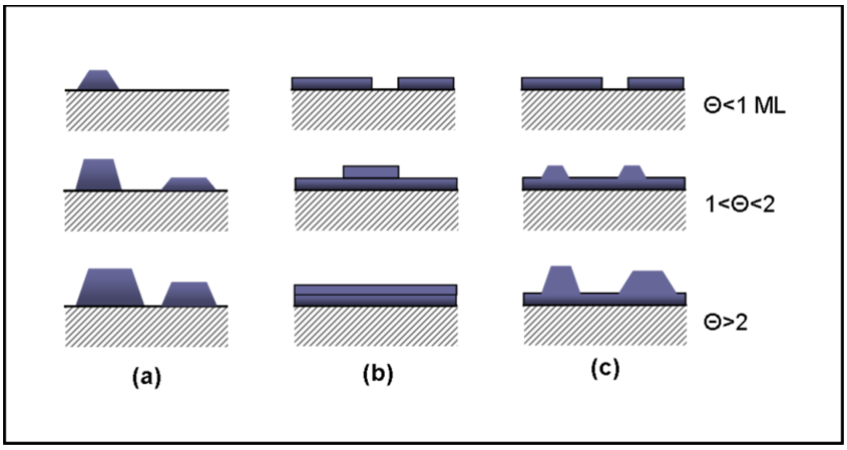


Figure 2: Cross-section views of the three primary modes of thin film growth:(a) Volmer-Weber(VW), (b) Frank-van der Merwe(FM), (c) Stranski-Krastanov(SK). Each mode is shown for several different amounts of surface coverage, Θ

then the real quantity we need to consider to determine the morphology of film is just

$$\Delta\gamma = \gamma_{BV} + \gamma_{AB} - \gamma_{AV}$$

Here, γ_{AV} and γ_{BV} correspond to the surface energy density of the interface between thin film B and vacuum and interface between substrate A and vacuum. According to different $\Delta\gamma$ value, there are basically three categories of growth modes(like the case in Figure 2):
The layer by layer mode($\Delta\gamma < 0$), or Frank-van der Merwe(FM) mode
The islanding mode($\Delta\gamma > 0$), or Volmer-Weber(VW) mode
The layer plus islanding mode, or Stranski-Krastanov(SK) mode
($\Delta\gamma < 0$below the critical thickness, $\Delta\gamma < 0$ above the critical thickness)

2 Elementary mechanism of QSE

2.1 The arising of quantum growth mode

Normally, growing an perfect flat metal thin film onto the semiconductor substrate is very hard. As a result of the difference in atomic bonding(metallic bond versus covalent bond) and large disparities in surface diffusivity, metal film on semiconductor substrate tends to form some 3D island, even for the case when deposited material has perfect lattice constant match with the substrate. However, because of it's great potential as a testing ground for many theoretical models, research into the thin metal film growth has never stopped.
In 1996, Arthur R. Smith[1] find another kinetic process for metal-on-semiconductor epitaxial growth which is completely different from the traditional epitaxial methods such as MBE (molecular beam epitaxy). They grow silver thin film on the GaAs(110) surface following a

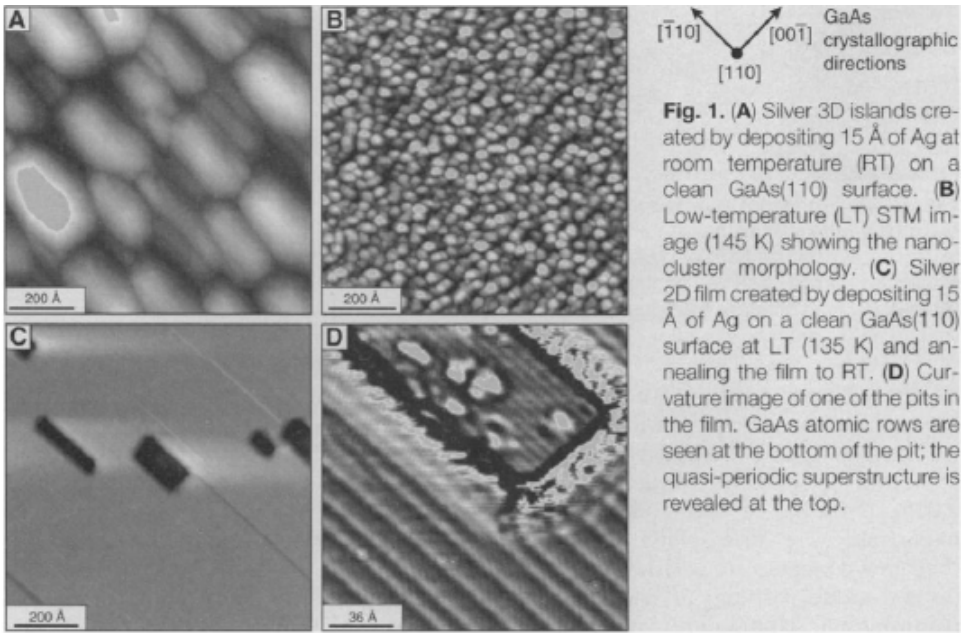


Figure 3: STM image of the Ag film[1]

two-step process, in which they first deposit Ag under low temperature(135K) and then anneal the sample slowly up to room temperature. What they find under low temperature from STM is a lot of nanoclusters not flat film or islanding form film, and after the slow annealing to room temperature they get flat film like Figure 3. They find that 15 Å(about 6 monolayer (ML)) is a favorable thickness for the thin film. If the amount of deposited Ag is not enough to cover the whole surface with 15 Å thick, the film will form some pits which directly extends down to the substrate, like the case in Figure 3(c) and (d) in order to make sure that other parts of the film have that preferential thickness. While if the amount exceeds the 15 Å amount, then the film tends to first form flat 15 Å thick film and then form some 2D island on top of it. People attribute this phenomenon to the size quantization of the itinerant electrons, which is the so-called "quantum size effect". And people also find similar phenomenon in some other metal-semiconductor thin film system, such as Ag/Si(111)[4], Pb/Si(111)[5] and Pb/Ge(100)[6], Pb/Ge(111)[7].

2.2 Starting from a very simple model

In order to have a conceptual idea of QSE, let's first have a quick look at a simple example —the "*particle in a box model*" as the case in Figure 4 below. In this one dimension case, because of the restrictions on the two sides, the energy levels of the particle in the well will split into discrete levels. If we consider the real thin film system as Figure 5(a), obviously it

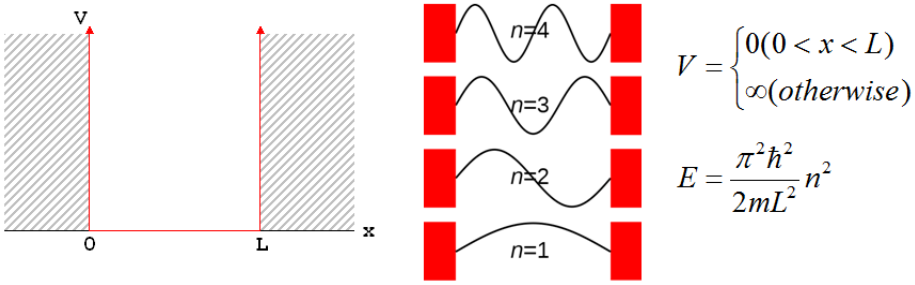


Figure 4: The infinite square well problem

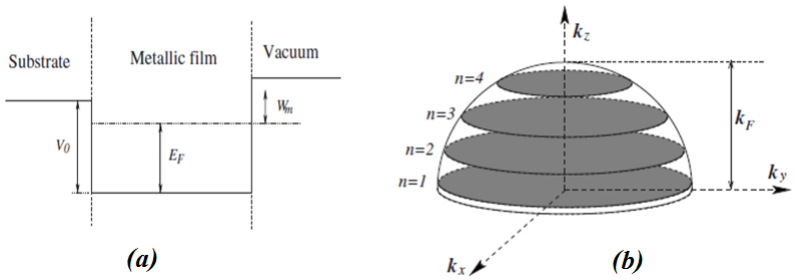


Figure 5: (a)The thin film system (b) the Energy subbandss of a metallic thin film under the simple"particle in a box" model[2]

has the similar environment. Actually, many theoretical physists apply the free electron model to this system, in which the thin film is regarded as a collection of free electrons, and the energy barriers in the two interface provide the potential wall so that the itinerary electrons in metal films are confined in the z direction which is perpendicular to the film surface.This restriction results in discrete energy levels associated with the so-called Quantum Well states[3]. While in the meantime, on the xy plane, we still have free electron like Bloch wave form wave function and corresponding energy level distributions(Figure 5(b)). And this discretization of the energy band leads to an osicillartory dependence of the film's total energy on its thickness. So, some certain thicknesses may be energetically more preferential.

Although it neglects the lattice potential and electron-electron interaction, it turns out that this simple model only works well for continuous films such as Pb(111) and Al(111), but is not so good for films consisting of well-seperated islands. And to the simplest case, the potential well could be an infinite potential well. If we want to consider the charge spilling effect, we could also treat the system as a finite potential well or we could also apply the lattice potential. But it turns out that these different potentials don't make any fundamental difference to the final result. And because we negelect the lattice potential and electron-electron interaction, this free electron model is too rough to predict which thickness is stable but we could get a pretty good estimation of the possible behavior of the film stability.

3 QSE and thin film stability

3.1 Theoretical criterion of thin film stability

As a given amount of certain material is deposited on a substrate, many different types of morphology can form. If we only consider the continuous film as seen in Figure 6, then during annealing at certain temperature, the film will have at least two routines of morphology change. Obviously, the driving force behind this change should be the thermodynamics: the system always try to reach a lower energy state. The configuration that is a local minimum in the system energy is relatively stable and will likely be the outcome of annealing.

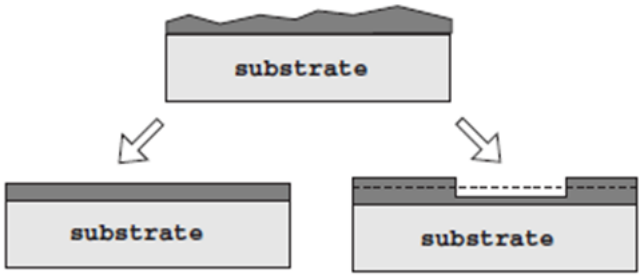


Figure 6: Two possible morphology evolution of continuous thin film upon annealing[2]

If we only consider the simplest case, then the film can become atomically flat or flat top islands which have two different heights. The atomically flat film on the left is possible only if when $E_t(left) < E_t(right)$. Here, $E_t(left)$ and $E_t(right)$ are total energy of two films at the bottom of Figure 6. If we assume the total contact area of the film with the substrate to be S, then the condition when an atomically flat film of L monolayers is stable when

$$E_s(L) \cdot S < E_s(L+1) \cdot (S/2) + E_s(L-1) \cdot (S/2)$$

Here, $E_s(L)$ is the surface energy per unit area.
If we define $d^2E(L) = E_s(L+1) + E_s(L-1) - 2E_s(L)$, then the criterion will become

$$d^2E(L) > 0$$

. For a thick film, the properties of film is more bulklike. That means the properties doesn't change much when we plus or minus one monolayer, so $|d^2E(L)| \ll 1$. Reversely, when $|d^2E(L)| \ll 1$, we can say that the film is more bulklike in terms of stability. Here, $|d^2E(L)| \ll 1$ only tell us that $E_s(L)$ is convex locally. To make the L monolayer thick film stable in the whole area, we need to have this relation valid globally. And fortunately, under the free electron model for metal film, $E_s(L)$ is usually convex globally.

3.2 Some theoretical calculation results under the free electron model

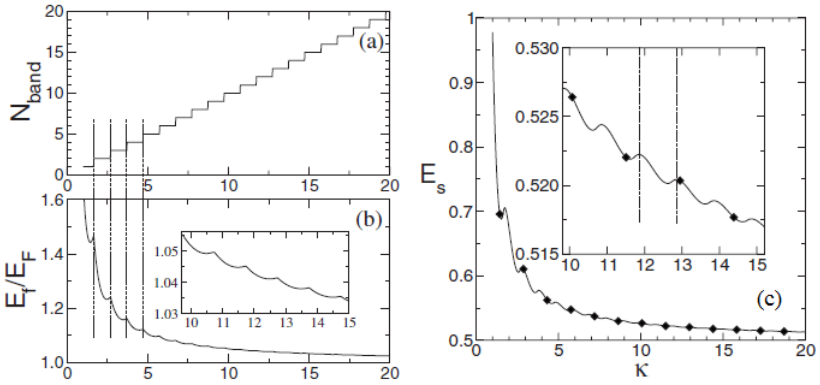


Figure 7: (a) Number of subbands below the Fermi surface (b) Fermi energy of the thin film E_f (c) Film interface energy E_s as a function of κ. Interfaces are modeled as infinite energy barriers. The inset shows the enlarged portion of E_s for large κ. The diamonds are the results for Pb(111) film. E_s is in units of $E_F k_F^2/4\pi$. $\kappa = dk_F/\pi$, where d is the thickness of film and k_F is the bulk Fermi momentum.[2]

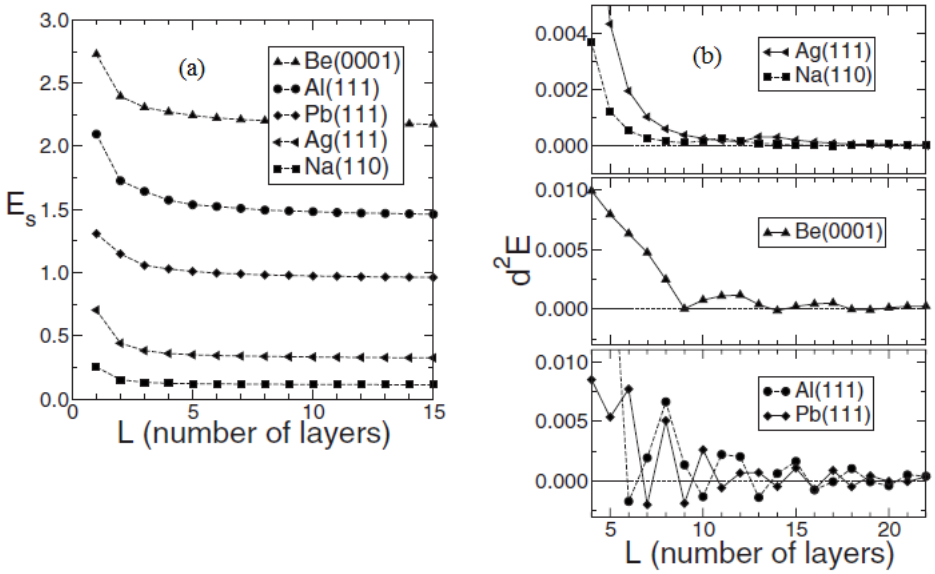
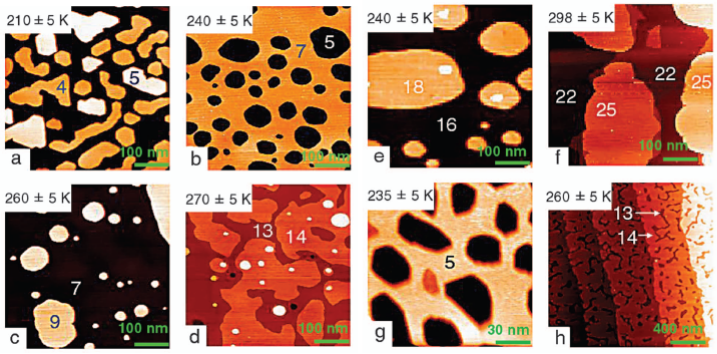


Figure 8: (a) Film interface energy E_s as a function of layer number L for metallic films: Be(0001), Al(111), Pb(111), Ag(111) and Na(110). E_s is in units of $eV/\mathring{A}^2$ (b) d^2E as a function of layer number for metallic films: Be(0001), Al(111), Pb(111), Ag(111) and Na(110). d^2E is in units of $eV/\mathring{A}^2$ [2]

Figure 7 is a plot of the oscillating behaviors of the Fermi level and the surface energy versus the increasing film thickness. Here, κ is not just a unitless quantity, it is also the total phase accumulated by the electron at the bulk Fermi level E_F travel back and forth inside the film.

The decreasing trends of Fermi level of thin film is easy to understand, because in the phase space the z component of wave vector is discrete, so in order to make the total number of electrons conserved, the corresponding Fermi level should be a little bigger than the bulk value. And with the increasing thickness of film, the difference between the discretized wave vector along the z direction become smaller and smaller, and finally the E_f value should be more or less the same as the bulk one E_F. We should also pay attention to the oscillating behavior in the plot. It is because of the sudden emergence of new subband without thickness changing. And there is another interesting phenomenon is that the oscillating period is around $\lambda_F/2$. We can also find this oscillating behavior in the plot of E_s.
Considering in the real case, the film thickness can only change one layer by one layer and not continuously, the plot of E_s in Figure 7(c), which is the universal surface energy trends for all metal films, to some extent is a little "imaginary". Because for different metals, the thickness of 1 ML is different, what we get in the real case for different metal films are just different sets of discrete points distributed along that "imaginary" curve. In Figure 7(c), the discrete points corresponds to Pb(111) thin film.
Actually, it is still hard to tell which thickness is stable and which is not. If we think about the stability criterion in the previous section, plotting d^2E could be a good idea, such as the result in Figure 8(b). As I mentioned before, the free electron model is only a rough model.
Although it can't predict exactly which thickness is stable and which is not, we can still get some valuable information about the stability trends from this model. For example, in Figure 8(b), we can see that the stability exhibit an even-odd oscillations around the horizontal axis. Actually, this fits the experimental result prefectly as below[7].



Interface	Observed Layer Thickness										
Si(111)7x7-Pb	5	7	9	11	13	14	16	18	20		
Si(111)(√3×√3)-α	5	7	9	11	13	14	16	18	20	22	25
Ge(111)(√3×√3)-α	5	7	9	11	13	14	16	18	20		

Figure 9: (a-f) STM image of Pb on Si(111)$\sqrt{3} \times \sqrt{3}$ (g)Ge(111)$\sqrt{3} \times \sqrt{3}$ (h) Si(111)

3.3 More examples of quantum film system and further discussion

Like I mentioned at the very beginning, there are also some other quantum film systems where the QSE plays an important role in the film stability. The Ag/Si(111)-(7×7) system in Figure 10 below is another good example for the quantum growth mode.

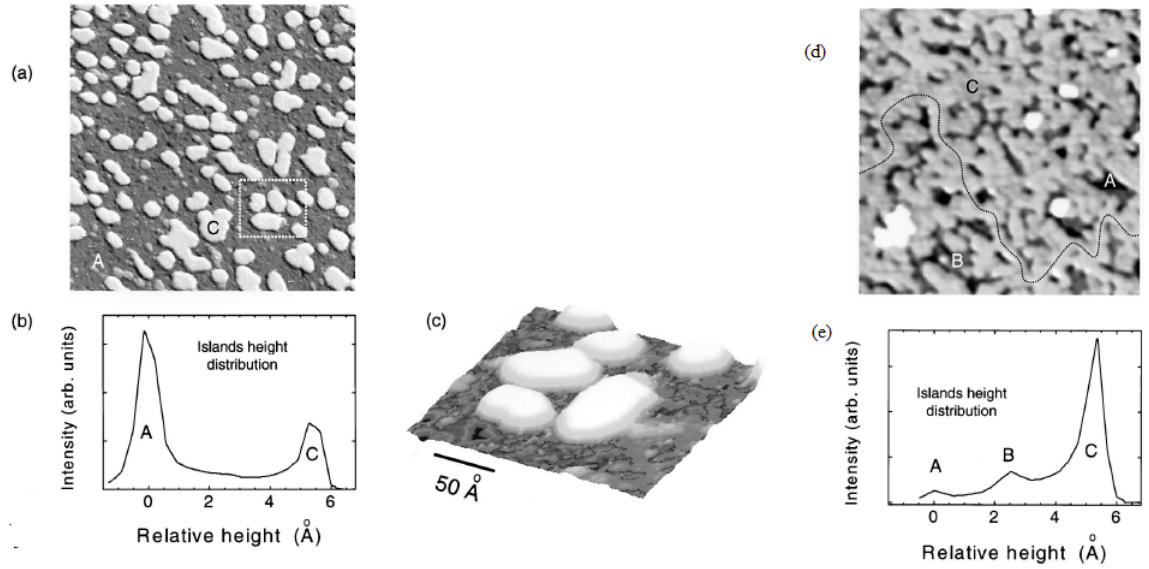


Figure 10: (a-c) STM image of 1-ML Ag film deposited on Si(111) at 150K and annealed to room temperature, (a) $1000 \times 1000\mathring{A}^2$, (b) Island height distribution, A represents the wetting layer and C represents the preferred island height, (c) 3-D view of area marked in(a); (d-e) STM image of 2.2-ML Ag film deposited on Si(111) at 150k and annealed to room temperature, (d)$1000 \times 1000\mathring{A}^2$, (e) Island height distribution[4]

Normally, RT Ag deposition follows the SK growth mode, but under this two-step growth routine, the atomically flat film is achieved and the preferred island height is 5.4 $\mathring{A}$. The difference between this system and the ones we discussed before is that the Ag atoms tends to first form a wetting layer. In Firgure 10(e), we have an extra peak B. The authors of the original paper say the peak intensity will decrease by either using a lower deposition rate at LT or annealing for longer time up to RT, so they assume this doesn't affect their conclusion on the preferred island height.

In summary, the quantum growth mode is a new growth mode, in which energy contribution of the quantized electrons confined in the metal overlayer can actually determine the morphology of the growing film, prevailing over the strain stress resulting from the lattice mismatch. This is actually the spirit of descriptions in the previous three sections, where we spent a lot of time

on the electron contribution in the surface energy behaviors. From the perspective of electron contribution, Zhenyu Zhang and Qian Niu pointed out that[8] three factors play important role in the film stability, the quantum confinement, the charge spilling effect and the interface Friedel Oscillation. The quantum confinement tends to stablize the flat film phase, the charge spilling effect around the substrate tends to destablize the flat film, and the interface induced Friedel Oscillation impose another modulation onto these two effects. These three factors compete with each other, and finally determines the film morphology.

Techniquely, of course, for the quantum film we discussed in the previous sections, we should first have small deposition amount, otherwise the film will be more bulklike. However, the most significant difference between this growth mode and the classical modes is the low temperture, when the system is far from thermoequilibrium. In the classical modes, the stress effect plays an important role in determining the thin film morphology. For Ag deposition in the examples I presented, the strain effect normally result in the SK growth mode. The two-step methods successfully circumvent this strain effect by using low temperature deposition, in which the deposited species initially just stay where it was deposited. And the subsequent annealing provides a mount of energy for the deposited species to reach a local energy minimum phase, the quantum film phase. For my opinion, the flat metal film phase on the semiconductor substrate is, to some extent, only a metastable state. Actually, if we consider the phase space for the thin film system, there are a lot of local energy minimum, so different routines may result in different phase.

4 Properties of quantum films

4.1 Lattice relaxation

The electronic charge density along the z direction oscillates in the quantum confined films with a period of $\lambda_F/2$ or $2k_F$, considering the simplest Coulomb interaction, it's easy to predict that ionic cores should be slightly displaced because of this new charge density distribution. But it turns out that this lattice spacing change is quite small and fluctuates about $-3 \pm 0.3\%$ around the bulk value. In experiment, there still lacks powerful experimental evidence of this effect either because the involvement of other effects or because of the large errors in fitting the results. Nevertherless, there has already been some theoretical results like the plot in Figure 11 as below[9].

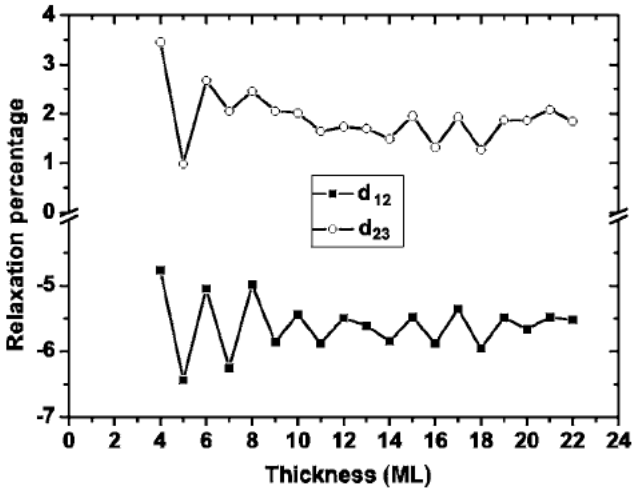


Figure 11: Interlayer spacing d_{12} and d_{23} of Pb(111) films on Si(111) substrates relative to bulk spacing[9]

4.2 Surface reactivity and corresponding catalytic properties

It is known that the surface reactivity of materials is size dependent. A typical example is the high activity of supported gold clusters of particular dimensions in CO oxidation[10], while we all know that bulk gold is fairly stable.

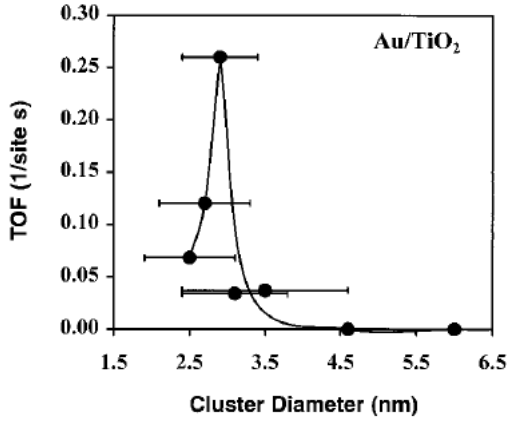


Figure 12: CO oxidation turnover frequencies(TOFs) at 300K as a function of the average size of the Au clusters supported on a high surface area TiO_2 support. The Au/TiO_2 catalysts were prepared by deposition-precipitation method, and the average clluster diameters were measured by TEM. The solid line serves merely t guide the eye[10]

Actually, the surface reactivity is usually related to the corresponding density of states, especially the density of states around the Fermi level. From the previous description of free electron model, such as Figure 5(b) and Figure 7(a), we know that when the film thickness increases, the number of subband will also increase. When the new subband going across the Fremi level, the density of states around the Fermi level will increase. Actually, people do find surface reactivity properties of thin film related to this process, such as Figure 13 and Figure 14[11]. In that experiment, people investigated the surface reactivity of Mg film in the oxidation process with different film thickness. And it turns out that the surface reactivity goes up to a maximum only when new subband or new quantum well states coming cross the Fremi level as indicated in Figure 13(c).

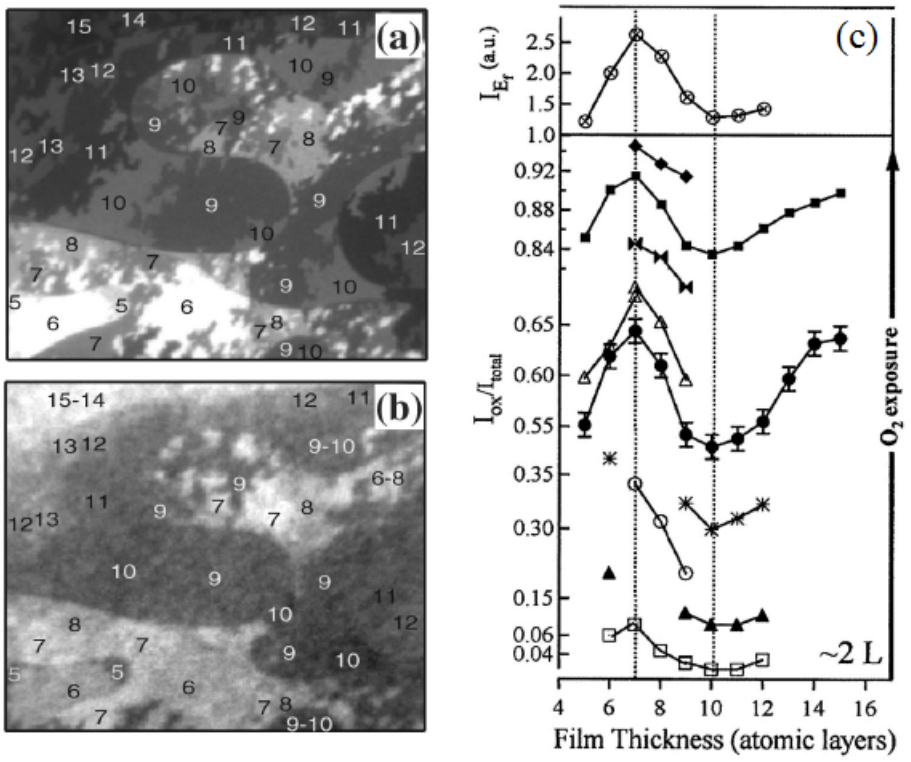


Figure 13: (Left)$6 \times 5\mu m^2$ images of a Mg film on W(110) substrate in an advanced growth stage.(a) 1.3 eV LEEM image of the surface: the indicated numbers are the corresponding island thickness before adsorption of O_2 (b) XPEEM image of the same Mg film after exposure of 9 L of O_2. The image is obtained by measuring the Mg 2p intensity of oxidized Mg (I_{Ox}) (c)Plots of the relative weight of the Mg 2p oxide component, I_{OX}/I_{total}, obtained in several experimental runs. Data indicated with the same symbols correspond to the same O_2 exposure. (Upper panel) Photoemission intensity at the Fermi level measured for different microregion thickness before oxygen exposure with energy resolution of 0.25 eV[11]

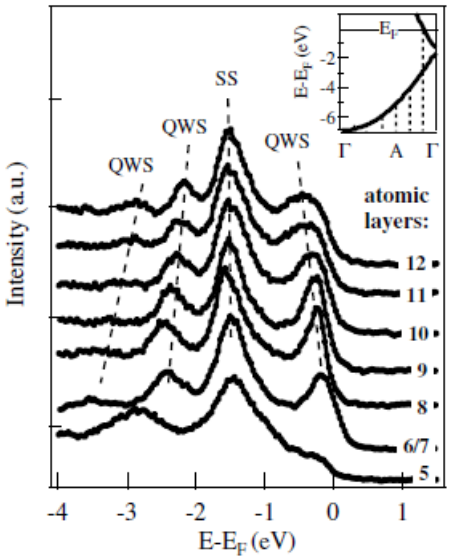


Figure 14: Valence band spectra obtained from microregions wih the indicated thickness[11]

5 Conclusion

Quantum growth mode is a new thin film growth mode, in which the quantum confinement of the itinerant electrons plays an important role on the film stability. With this method, atomically flat metal film on the semiconductor substrate becomes possible and also a lot of interesting properties come out, such as the surface reactivity change with different film thickness and the lattice relaxation of the film. Actually, people also find some other interesting phenomena, such as the superconductivity of metal thin film, because of the limited time, I can't give more introduction on that topic.

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