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Comments on some experimental measures of the non-metal to metal transition in thin films

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A brief review is presented of experimental indicators of metallicity and the metal–non-metal transition, with particular emphasis on studies of thin films. Problems of definition and measurement are emphasized.

Keywords: thin films; experimental methods; probes of metallicity

1. Introduction

There is a continuing need for both theorists and experimentalists to address what the various probes of metallicity are actually measuring. One of the great problems in studying the non-metal to metal transition in thin films and overlayers is actually finding some definitive experimental probe of the transition and, perhaps more importantly, understanding what that particular measure of metallicity means. In this area of research a crucial question is, What is the definition of metallicity? The question is not trivial; different experimental probes may measure different aspects of the electronic structure through a non-metal to metal transition and may not always be directly related. Thus, let us summarize this issue by providing a simple overview of some different measurements of the non-metal to metal transition and their strengths and weaknesses.

2. Experimental indicators

(*a*) *Conductivity*

One observes for metals that the resistance increases and the conductivity dereases with increasing temperature. For semiconductors, the conductivity increases and the resistivity decreases with increasing temperature (a negative as opposed to a positive coefficient of resistivity that is observed with metals). There are some bulk materials for which this criterion of conductivity fails; liquid zinc is a classic case (Sinha *et al.* 1989; Roll & Motz 1957). Here is a metal with a negative coefficient of resistivity with temperature.

The conductivity definitions of metallicity are difficult to apply to free clusters or two dimensional systems (or at surfaces). One cannot attach wires to a small cluster of a few atoms. Since free standing monolayers or even two monlayers are difficult to fabricate, in practice, the conventional means of determining metallicity (conductance or sheet resistance) must be reconsidered for overlayers and thin films on a substrate. The substrate, even a semiconducting substrate, will more than dominate any measurement if the overlayer is only a couple of atoms thick. Furthermore, it is also very difficult to connect wires or probes to a monolayer film; almost

any current applied will destroy percolation. Metallic and semiconducting thin films, submonolayer to multilayers thick, have recently been characterized on insulating Si(111) (Schad *et al.* 1992; Luo *et al.* 1994; Jalochowski & Bauer 1988; Hasegawa & Ino 1992; Rubenstein *et al.* 1988; Fischer *et al.* 1980; Kimberlin & Tringides 1995), but the most recent studies suggest that these four point probe measurments are dominated by the silicon depletion layer or subsurface region of the substrate and not the overlayer (Kimberlin & Tringides 1995). For systems where the non-metal to metal transition is temperature dependent, the coefficient of the conductivity may be also 'swamped' by the change in metallicity or a change in density independent of metallicity. This would invalidate this as a measure of the metallicity, particularly close to the transition.

There are other complications with conductivity as applied to the metallicity of thin film overlayers and deposited clusters. The non-metal to metal transition will often occur for film thicknesses between half a monolayer and two monolayers. Such films are seldom continous in practice and on some surfaces, the overlayer will not grow one complete layer at a time (layer by layer growth) so percolation as a concept must be used cautiously, even though the data may be consistent with percolation models. A surface covered by islands may not fufill the convention definition of two dimensional percolation, nonetheless each island itself may be metallic in much the same way that small free clusters of atoms can be metallic. It is true that the surface photovoltage can be used to probe the non-metal to metal transition (Hamawi & Walldén 1992; D. Li *et al.* 1992; Musatov & Smirnov 1992; Waddill *et al.* 1990) effectively by probing the surface conductivity of the semiconductor substrate following thin film or cluster deposition. Nonetheless, conventional measures of conductivity, as well as indirect measures of surface conductivity (like the surface photovoltage), could fail to detect the non-metal to metal transition for many overlayer and thin film systems.

(*b*) *The Drude tail*

With a metal, very small energy excitations across the Fermi energy become possible whereas for a semiconductor, there is an appreciable gap between the valence band edge and the conduction band edge. These small excitations in a metal should be apparent in electron energy loss spectroscopy, infrared spectroscopy (Gayman *et al.* 1993) and Raman spectroscopy (Bozovic *et al.* 1994; Gupta *et al.* 1996) as an inelatic scattering processes that results in line broadening. This line broadening can effect photoemission peaks shapes as well, at least in principle. This is the Drude tail. The existence of a Drude tail is not in question, but a number of experimental effects can lead to similar spectral changes making it difficult to identify the Drude tail. Defects and structural phase transitions can lead to defect scattering thus masking the effect of the non-metal to metal transition even in high resolution electron energy loss. The non-metal to metal transition is often accompanied by a structural transition, but clearly not all structural transitions are accompanied by a non-metal to metal transition. Thus scattering effects due to structural transitions and defect scattering are not good indicators though they can produce profound spectroscopic effects.

Vibrational damping of a weakly bound adsorbate (such as CO) due to coupling with the substrate electron hole pairs is could occur. Such studies suggest that the transient response of a vibrationaly excited probe molecule could be used to investigate the non-metal to metal transition of the underlying substrate surface. Clearly,

the substrate–molecule interactions would have to be taken into account. In particular, the chemical bonding of the CO or any molecular adsorbate would tend to localize the surface state electrons. Thus how one would account for the interaction of the 'probe' adsorbate with the substrate is at present not very clear. A study probing essentially this same physics more directly investigated the antiabsorption resonances for alkali metals on Cu(111) (Hoffman *et al.* 1994). The evidence suggested a pinned charge density wave for the alkali overlayer. This pinned charge density wave, in turn, suggests that alkali metal overlayers on Cu(111) could undergo a non-metal to metal transition. Unfortunately, there is little other *compelling* experimental evidence for alkali metals on copper surfaces with both supporting and contradictory results available.

(*c*) *Plasmons and optical properties*

Clearly a metal has a much larger dielectric response than a non-metal. This is a result, in part, of the shift in the optical gap, alluded to above and can be correlated with the non-metal to metal transition (for example in supercritical fluids (Hensel 1990; Likalter 1992) or the CMR manganese perovskites (Kaplan *et al.* 1996; Okimoto *et al.* 1995; Uchida *et al.* 1996)). One problem is that as the gap decreases, longer and longer wavelength light is required to generate an optical conductivity near the critical gap energy, and avoiding absorption from water vapour, widows and optical components becomes increasingly difficult, even when a suitable infrared source can be found. If the material investigated is a thin film, then these measurements are again dominated by the large signal generated by the substrate where most of the optical absorption generally occurs.

The optical gap also often translates into the dramatic change of the second harmonic signal as well across the non-metal to metal transition (Arekat *et al.* 1993). In the case of the second harmonic signals problems still exist. First of all, this technique, by its very nature, is surface sensistive. Second, the wave length used to generate the second harmonic signal is finite and typically of the order of a couple of electron volts (usually visible lasers are used for this spectrsoscopy). Thus spectra can be dominated by excitations across a gap also of several electron volts, providing a signal characteristic of a metal for a system which is patently not metallic (Hollering *et al.* 1990). The damping by the substrate of second harmonic signal has also been observed for sodium on Cu(100) (Persson & Dubois 1989), a system related to the antiabsorption resonance of CO mentioned above (Hoffman *et al.* 1994).

Plasmons have also been used as a signature of the non-metal to metal transition. Ideally, plasmons should be characteristic of metals. Unfortunately many non-metals (silicon for example) exhibit strong plasmon losses in electron and optical spectroscopy, while a number of metals have very strongly damped plasmons (copper for example). For thin films the substrate can again be a problem. Nonetheless, the plasmon satellites have been used to suggest a non-metal to metal transition for Na on Al(111) (Seymour *et al.* 1989). This result has modest support from valence band photoemission (Horn *et al.* 1988) though this result is not supported by electron energy loss spectroscopy (Liebsch 1991) and furthermore, damping and reconstruction effects (Andersen *et al.* 1991; Stampfl *et al.* 1992; Schmalz *et al.* 1992) have not been eliminated or accounted for in these various spectrsocopies of alkali metals on Al(111). Indeed, the first experiment (McRae *et al.* 1969) to suggest that a metal overlayer on a metal substrate might undergo a non-metal to metal transition was based upon plasmon losses, and was an important concept, though no supporting

experimental work for that system was ever found. For even non-metallic free Hg clusters, a Mie plasmon can be observed (Haberland *et al.* 1992, 1993).

Somewhat more successfully, the plasmon loss intensity was used to identify the non-metal to metal transition for Mg, Sr and Ba on Mo(112) and Re(1010) (Katrich *et al.* 1994) and Alkali metals on Si(100) (Aruga *et al.* 1984; Tochihara 1983; Tochihara & Murata 1982). For the Mg on Mo(112) and alkali metals on Si(100), the non-metal to metal transition has been confirmed by a variety of other techniques.

(*d*) *Screening and excitons*

The Mott criterion (Mott 1967, 1990; Mott & Davis 1971) for a non-metal to metal transition includes the disappearance of bound states as the electron density increases, the Coulomb repulsion energies fail to keep the electrons bound to ion cores and the free electron approximation becomes, at least partly, valid. This can be generalized to higher excited states (Popielawski 1978) and core excitons (Dowben 1991; D. Li *et al.* 1992; Zhang *et al.* 1994*b*, 1995*a*, *b*). One of the really good examples of this phenomena, for a thin film, is the washing out of the Xe Wannier states in mercury–xenon mixtures (Raz *et al.* 1972) at 55

Exciton formation and decay can also be observed in electron energy loss (EELS) as has been done in the case of the alkali metals on GaAs(110) (DiNardo *et al.* 1990) as well as for the alkali metals on copper surfaces (Aruga *et al.* 1986; Lindgren & Walldén 1980). In the case of Cs/GaAs(110) (DiNardo *et al.* 1990), this is to be expected since the system appears to resemble a Mott insulator at low coverages.

Similar phenomena can be observed using resonant photoemission (Dowben 1991; Dowben & LaGraffe 1990; D. Li *et al.* 1992; Park *et al.* 1995; Zhang *et al.* 1993, 1994*a*, *b*, 1995*a*, *b*), where instead of forming a valence exciton, a core exciton is created (D. Li *et al.* 1992). In the case of mercury, this measure of the non-metal to metal transition can be compared (Dowben *et al.* 1991, 1996; D. Li *et al.* 1992; Zhang *et al.* 1993, 1994*a*) with resonant photoionization results of free Hg clusters (Bréchignac *et al.* 1988) as well as the results from Hg–Xe mixtures (Raz *et al.* 1972). The resonant photoemission intensity (I) can be, in principal, related to the the screening parameter ls (the inverse of the screening length) (D. Li *et al.* 1992). This technique has been criticized, in the past, for the absense of theoretical support for this spectroscopy, but there are very effective simple models for this probe of core exciton formation and decay (D. Li *et al.* 1992; Zhang *et al.* 1995*a*, *b*).

This technique of resonant photoemission to probe screening has now been tested against other, more conventional, measures of the non-metal to metal transition (McIlroy *et al.* 1996). This has confirmed that the technique is indeed a powerful tool in the arsenal of spectroscopies useful for probing the non-metal to metal transition. The technique does have limitations.

The intensity changes in resonant photoemission cannot be compared to any 'standard' as yet. This means that a change in metallicity can be observed, but it may not necessary correspond to a non-metal to metal transition. The resonant signature must be separated from the background; thus one cannot study a system like Na on Si through the non-metal to metal transition by studying the silicon resonance. Above all, this is a technique which requires a tunable light source in the VUV, and that means a synchrotron light source. The monochromator performance is thus very important—one has to run the electron energy analyser together with the monochromator—and one has to be very careful about second order light effects and light flux normalization. More theoretical support for this technique would be very welcome.

(*e*) *Core level spectroscopy*

While X-ray photoemission spectroscopy is not a direct measure of metallicity, the apparent core level line shape and binding energy has been used indentify non-metal to metal transitions. The apparent core level line shape and binding energy is strongly affected by final state effects (Fedorov *et al.* 1994; Ortega *et al.* 1994) as well as affected by plasmon losses (Seymour *et al.* 1989), Drude tail broadening, and screening effects (Riffe *et al.* 1992). As such, the spectroscopy of the deep core levels may be influenced by a non-metal to metal transition. For Li on Be(0001), there is certainly a binding energy shift that accompanies the non-metal to metal transition (Watson *et al.* 1994), and both the line shape and binding energy of the K 3p level are observed to change through the non-metal to metal transition for K/Si(100) 2×1 system with increasing potassium coverage (Riffe *et al.* 1992). Unfortunately, these spectroscopic signatures can also result from changes other than a non-metal to metal transition, or result in changes so small that the core level line shape and binding energies are dominated by other phenomena. To demonstrate this point, a study of the core levels of Mg overlayers, as a function of coverage, was undertaken. This system, by every other measure, undergoes a non-metal to metal transition (Katrich *et al.* 1994; Zhang *et al.* 1994*b*, 1995*a*, *b*), yet there is no discernable change in the Mg core levels across the non-metal to metal transition.

For shallow core levels, in particular for the Hg 5d core levels, the line shape and binding energy can be very significant in part because these core levels can develop weakly dispersing bands or contribute to the valence band structure (Dowben *et al.* 1987, 1988*a*, *b*, 1990*a*, *b* 1991; D. Li *et al.* 1992; Onellion *et al.* 1986, 1987; Singh *et al.* 1994; Zhang *et al.* 1993, 1994*a*). This can be a very strong measure of the non-metal to metal transition (D. Li *et al.* 1992; Singh *et al.* 1994) and can be correlated with other measures on the non-metal to metal transition (D. Li *et al.* 1992) and theory (Singh *et al.* 1994).

(*f*) *Density of states at the Fermi energy*

A metal must have a density of states at the Fermi energy. Indeed, a metal is a material with a partially filled band. Such a test for metallicity is very common (Smith 1997). The prevalence of this measure of the non-metal to metal transition is exemplified in the study with now classic non-metal to metal transition overlayer systems: alkali metals on Si(100) (Ciraci & Batra 1988; Johansson & Reihl 1991; Enta *et al.* 1989; Nishigaki *et al.* 1990; Michel *et al.* 1992; Reihl *et al.* 1992) and alkali metals on GaAs(110) (Cao *et al.* 1989; Heskett *et al.* 1991; Reihl *et al.* 1991; Whitman *et al.* 1991; Wong *et al.* 1989).

A variety of techniques can be employed to probe the density of states at the Fermi level including photoemission (UPS and ARUPS) (Cao *et al.* 1989; Enta *et al.* 1989; Johansson & Reihl 1991; Heskett *et al.* 1991; Horn *et al.* 1988; Katrich *et al.* 1994; Kevan & Stoffel 1984; D. Li *et al.* 1992; McIlroy *et al.* 1996, 1997; Michel *et al.* 1992; Muscat & Newns 1979; Olsen *et al.* 1995; Reihl *et al.* 1992; Ventrice *et al.* 1992; Walldén 1985; Watson *et al.* 1994; Weitering *et al.* 1997; Wong *et al.* 1989; Zhang *et al.* 1994), inverse photoemission (IPES) (Johansson & Reihl 1991; McIlroy *et al.* 1996, 1997; Reihl *et al.* 1991; Watson *et al.* 1994; Weitering *et al.* 1997), metastable quenching (de-excitation) spectroscopy (MQS) (Nishigaki *et al.* 1990; Woratschek *et al.* 1985) and even scanning tunnelling microscopy (STM), by taking current versus tunnelling voltage curves (Whitman *et al.* 1991). One of the major failings of all of these techniques is again they are surface sensitive. If one is trying to determine bulk

properties, there is the implicit assumption that the electronic structure of the surface region is representative of the bulk material, not necessarily a valid assumption (Liu & Klemm 1994; McIlroy *et al.* 1996; Waldfried *et al.* 1997).

The situation is not much better if one is interested in a non-metal to metal transition at the surface or for a very thin film. One of the major problems, particularly for overlayers on a metal substrate, is the need to subtract or account for the contribution to the density of states from the substrate. Subtraction of the substrate signal is certainly one method of dealing with the contribution from the substrate (Watson *et al.* 1994; Zhang *et al.* 1994*b*), but this is not an entirely appealing approach. Many assumptions and questions must be addressed to make this background subtraction possible, for example: how does the substrate signal contribution change as the overlayer coverage is increased? One can improve upon the surface sensitivity of the spectroscopy to the density of states at the Fermi level by applying metastable de-excitation spectroscopy of He^* atoms (MQS) (Nishigaki *et al.* 1990; Woratschek *et al.* 1985) or by doing photoemission at a photon energy close to the plasma resonance (Katrich *et al.* 1994; Plummer *et al.* 1994).

Another major problem is that the density of states, say in photoemission, may be very close to the Fermi energy, yet there is no dispersion across the Fermi level (Binns & Norris 1991; Binns *et al.* 1984; Dowben *et al.* 1991). Thus changes in the density of states may not be representative of a change in metallicity (D. Li *et al.* 1992) unless one undertakes a careful band mapping. An example of this occurs with mercury overlayers where the apparent agreement between experiment and theory is misleading (D. Li *et al.* 1992) because of a lack of dispersion of the state near E_f. To address this problem, the experimental method of choice is to undertake a careful band structure mapping using either angle resolved photoemission or inverse photoemission (ideally both (Reihl *et al.* 1992; Watson *et al.* 1994)) and actually determine the Fermi level crossings, if any.

(*g*) *Fermi level crossings*

As indicated above, a metal must have a band crossing the Fermi level, while a non-metal will not. One of the most impressive examples of this has been the angle resolved photoemission studies of thallium chains on Cu(100) (Binns & Norris 1991) where the data suggests that the overlayer undergoes a Peierls distortion with decreasing temperature, resulting in a non-metal to metal transition. While coverage dependent band mapping have been undertaken to some extent for the non-metal to metal transition of alkali metals on Si(100) 2×1 (Enta *et al.* 1989), lithium on beryllium (Watson *et al.* 1994), the most detailed effort of this sort has been the study of the non-metal to metal transition of Mg overlayers on Mo(112) (Zhang *et al.* 1995*a*, *b*).

The problems with such experimental band mappings are numerous. Again, the difference between the possible substrate band structure and the band structure at the surface or near surface region must be taken into account in this case. For complex materials like the perovskites this will be very difficult (Liu & Klemm 1994; McIlroy *et al.* 1996; Waldfried *et al.* 1997). For simple systems, like 'metal' overlayers, the band mapping is actually easier than with just a simple assessment of the change in the density of states at the Fermi level, with a sufficiently large overlayer and substrate data set. This occurs in part because many of the assumptions or questions can be addressed by direct analysis of the data. Such questions might remain unresolved in the case of the wave vector integrated density of states at the Fermi level. Taking

a complete enough data set to construct an experimental band structure can be a tedious and time consuming process, thus explaining why band mapping are typically done for fewer coverages, concentrations or temperatures near or across a non-metal to metal transition than is the case for many of the techniques described above.

The most serious problem with determining the Fermi level crossings from an experimental band structure has been the limited resolution, of angle resolved photoemission and inverse photoemission, in both momentum and energy. For complex materials with a very large unit cell, the Brillouin zone becomes very small. the end result is that one samples a very large part of the Brillouin zone in experiment. This tends to make the band structure disperse less than may really be the case; the experimental resolution may artificially make a metal look like a non-metal. Improvements in light sources and electron spectrometers are being made that address this problem, but only to a limited extend. The resolution is still always limited by the fact that experiment is undertaken at finite temperature, thus leading to thermal broadening. Furthermore any electron spectrsocopy is dominated by final state effects, leading, as indicated above, to a large number of complications.

From experimental band structure mapping it is also possible to determine the electron effective mass. The effective mass of electrons is expected to dramatically change near the non-metal to metal trasition (Brickman & Rice 1970; Continentino 1992; March *et al.* 1979; Ramakumar *et al.* 1994; Santoro & Giuliani 1989; Yarlagadda & Giuliani 1994; Vollhardt 1984). Thus the change in the electron effective mass can be a good measure of the non-metal to metal transition. Success of the measurement is not, however, inevitable.

(*h*) *Work function and ionization potential*

These two techniques are obviously related to the establishment of a density of state near the Fermi energy. In practice, using the work function to establish the non-metal to metal transition is widespread (Aruga *et al.* 1986; Arekat *et al.* 1993; Castro *et al.* 1990; Enta *et al.* 1989; Katrich *et al.* 1994; Nishigaki *et al.* 1990; Oellig *et al.* 1988). Nonetheless, the work function minimum is not actually a good measure of metallicity. While the surface potential does become demonstrably more flat when the system goes metallic (W. Li et al 1992), unfortunately surfaces tends to undergo a stuctural change near the non-metal to metal transition, and structural changes in general can lead to a dramatic change in work function (Smoluchowski 1940). Qualitatively, the more open the surface structure, the smaller the work function, and this can be the dominant effect (Lang 1973). Thus it is not at all clear what the work function change actually means in terms of the non-metal to metal transition.

Work function measurements themselves have an inherent problem: different ways of measuring the work function (Kelvin probe or vibrating capacitance methods, retarding potential diode methods, photoemission, photoemission of adsorbed xenon, etc.) provide different values for the work function that can differ by more than 50 meV. This flaw rests not with the experimentalist, but with the experiment—different methods for measuring work function measure different things—a problem akin to different final state effects in photoemission.

For free clusters, the corresponding measurment is the ionization potential (Haberland *et al.* 1990; Rademann *et al.* 1987; Ruppel & Rademann 1994). Unfortunately, for this to be a more precise measure of metallicity it must be clear where the chemical potential of a free cluster rests. This is an issue of quite some debate.

3. Summary

What is clear from the above discussion is that a number of probes must be applied to the study of the non-metal to metal transition if one is to avoid being misled; there is no single experimental measure of metallicity without some drawback. Further, there is a need for more and better probes of the non-metal to metal electronic phase transition, though this discussion has only touched upon a few. In addition to the various experimental difficulties, there is also the difficulty of the transition itself. For many systems that undergo a non-metal to metal transition, it is clear that on one side it is metallic and on the other side of the transition the material is metallic, well away from the transition. Unfortunately, often there is a transition region, a 'grey region' if you will, between what is clearly non-metallic and what is metallic. Despite these failings of experiment—and both experimentalists and theorists should be well aware of the numerous failings of experiment—some very unusual examples on non-metal to metal transitions have been found (Plummer & Dowben 1993; Plummer *et al.* 1994; Dowben *et al.* 1996).

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