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Plasmons: quanta for micro-region temperature measurement

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An analysis is made of the shifts in the plasmon loss energies for a 1 keV electron beam scattered from pure tin as a function of temperature in ultra-high vacuum. The plasmons in tin are free-electron like and the thermal shifts are shown to arise from the volume expansion and consequent reduction in electron density as the temperature rises. The shifts for the volume plasmon of 0.49 meV K^{-1} in the solid state, and 0.60 meV K^{-1} in the liquid state, may be measured fairly readily to an accuracy better than 10 meV and hence provide a temperature measurement to better than 20 K. In the study of solid surfaces in an ultra-high vacuum scanning electron microscope, by a choice of electron beam energy, this method may be used to define the temperature in the outermost 1 nm at a solid surface with a lateral region limited only by the electron probe size. This may be less than 100 nm in modern surface analysis instruments and involve power of less than 10 nW. In the study of thin films by transmission electron microscopy, the temperature may be determined with a spatial resolution close to that of the imaging and involve even lower power inputs than for solid surfaces.

1. Introduction

The surface analysis of materials at elevated temperatures is important in studying reactions with the local environment or in studying compositional changes resulting from diffusion processes [1–3]. Furthermore, one can envisage elevated temperature situations in which the sample is not mounted on a controlled and monitored heating stage but has local heating as a result of part of the experiment. For instance, unintended heating may occur in samples involved in high fluence ion bombardment studies or where high flux probe beams are used to improve the sensitivity to certain measurements. On the other hand, an example in which the heating is not "accidental" occurs with integrated microcircuits. Under operation, these develop elevated temperatures in very small, localized regions. One cannot measure the temperature by optical pyrometry as the temperature is too low, nor yet again by thermocouple as the thermal fluxes are too low and the regions to be monitored too localized. A possible method for determining the temperature in such micro-regions is reported here, arising from a project involving interfacial reactions between solid and liquid metals.

In the present work we show that the sample temperature has a simple and easily understood effect on the volume plasmon energy in tin so that the latter may be used to define the temperature in a film with a thickness greater than the four atom layers necessary to sustain the plasmon oscillations [4]. The method has several unique factors which make it attractive, (i) the analysis volume may be limited to 100 nm by 100 nm by 1 nm depth, located and defined in a scanning electron microsope (in the scanning transmission electron microscope, STEM, the localization may be reduced to 5 nm by 5 nm); (ii) the method is contactless; and (iii) the thermal load can be less than 10 nW. An equivalent load using thermocouple wires would require wire diameters below 100 nm!

A number of previous studies of the effects of temperature on the plasmon energies exist. In a recent review, Raether [4] notes that shifts in the plasmon energies as a function of temperature and on melting in metals are in agreement with those calculated from lattice expansion and density changes. However, if we look at the data in which the temperature dependence is determined we find the measurements have a relatively poor precision.

Meyer [5] reports a shift of 0.58 ± 0.07 meV K^{-1} for the volume plasmon of aluminium compared with a predicted value of 0.53 meV K^{-1}, but with some scatter in the data. The correlation with lattice expansion is within experimental error, but if the energy of the volume plasmon is used in the reverse sense to determine temperature, the individual data points would lead to a root mean square (r.m.s.) uncertainty of 91° C for temperatures in the small range from 25 to 350° C. Powell [6] shows the data for the volume and surface plasmon losses from a 9 keV electron beam reflected from bismuth over the temperature range 25 to 600° C. The volume plasmon data are consistent with the lattice expansion on heating and a lattice collapse on melting, but individual data points again lead to an r.m.s. uncertainty of over 100° C when used to establish temperature. The surface plasmon data, however, showed an anomalous affect on melting. Later studies [7] of aluminium confirm that both surface and volume plasmons follow the predictions for lattice expansion in both the solid and liquid phases as well as the expansion on melting.

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However, here the scatters are worse and would lead to an r.m.s. uncertainty of around 200° C. Other studies of the temperature dependence of the characteristic energy losses from reflected low energy electron beams also exist, but all occur in the period prior to the development of modern surface analysis techniques. Thus, studies such as that of Apholte and Ulmer [8] show results that are variable and not systematic between single and multiple losses, perhaps due to uncontrolled contamination or segregation of bulk impurities. It is not clear from all this earlier work whether the scatters arise from simple considerations such as the signal-to-noise ratio, instrumental stability or a method to define the peak position accurately, which may all be overcome in modern instrumentation, or whether they arise from intrinsic inhomogeneities in the material such as strains which vary from grain to grain in crystalline materials, variations in surface porosity or very low levels of variable contamination, which could not, in practice, be removed. Thus, it is not known if the uncertainties arise from material variability or instrumental measurement precision.

2. Theory

The theory of plasmon excitations is covered well in Raether's early review [9]. For our present purposes we may take the simplest theory and note that the volume plasmon energy for a free electron metal of electron density, n, is given by [9]

$$\hbar w_p = \hbar \left(\frac{ne^2}{\varepsilon_0 m} \right)^{1/2} \quad (1)$$

where $\hbar w_p$ is the plasmon energy, e is the electron charge, m is the electron mass, and ε_0 is the permittivity of free space. The surface plasmon energy at a flat surface is simply $\hbar w_p / 2^{1/2}$ in this free electron approximation. For a given structure, the only temperature-dependent term is n, so that the temperature dependence of the plasmon energy is described by [5]:

$$\hbar w_p (T) = \hbar w_p (0) (1 - \tfrac{3}{2} \alpha T) \quad (2)$$

where α is the coefficient of linear expansion. The surface plasmon energy may be described by an analogous equation. Values of α for polycrystalline tin are 23.5 p.p.m. up to the melting point at 505 K and 29.2 p.p.m. for the liquid above 505 K [10].

Equation 1 may also be used to determine the shifts in plasmon energies due to the lattice dilation on melting. Numerically this is derived from the densities of the solid and liquid at the melting point given, respectively, as 7190 and 7000 kg m^{-3} [10].

3. Experiments

The experiments were performed in a VG Scientific ESCALAB II system with a LEG500 electron gun capable of 50 nm resolution at 20 keV. The sample, a freshly cut piece of Johnson Matthey Specpure tin of approximately 2.5 mm diameter, was placed in a small tantalum boat attached to the top of a calibrated heatable sample stub supplied with the instrument. The stub was introduced to the UHV and heated to about 600° C on the sample manipulator. After sputtering with 4 keV argon ions the liquid tin surface was clear of detritus, as monitored by the scanning electron microscope (SEM) facility, and was free of impurities as measured by Auger electron spectroscopy (AES). No contamination due to tantalum was observed nor did problems arise from evaporation of tin, which has an extremely low vapour pressure, even in the molten state [11].

Electron energy loss measurements of up to 50 eV were recorded using a 1 keV electron beam for various sample temperatures in the range 25 to 410° C. For defining the plasmon shifts accurately, an analyser resolution, $\Delta E/E$, of 0.02% (Retard ratio of 20 and 1.5 mm slits) was chosen. To check that the spectrometer was not affected by magnetic fields from the "non-inductively" wound stub heater, observations were made of the stability of the SEM image as the heater current was scanned through the full range. The SEM image shift was found to be less than 1.5 μm indicating a very low stray magnetic field.

As may be seen from Equation 2, an accuracy of ± 20 K requires an accuracy in the measurement of the losses of ± 10 meV. The 1 keV electron beam setting of the VG Scientific ESCALAB II would not be expected to have a long-term stability of this order and so spectra of the plasmon losses and the elastic peak were recorded as the sum of a number of rapidly scanned spectra involving 500 channels with a step size of 0.05 eV and an individual spectrum time of 50 sec. The spectra were recorded in the pulse counting En (E) mode.

After melting, the tin adopted a bead shape. Small shifts in the electron beam position then allowed measurements to be made at glancing incidence or at steeper angles in order to identify the surface and bulk plasmons. Measurements of the plasmon shifts as a function of temperature were then made at an angle of incidence around 45° which is typical for high spatial resolution studies.

4. Results

Electron energy loss spectra showing the plasmons for solid tin at 25° C, and liquid tin at 410° C for both glancing incidence and 45° incidence, are shown in Fig. 1. For the solid the two losses occur at 14.06 and 9.96 eV, respectively.

The energy loss spectra of the liquid at 410° C show two peaks with similar relative intensities as in the solid but with energies of 13.79 and 9.82 eV. The peaks shown in Fig. 1 are fairly broad and it is not easy to define the peak centre to sufficient accuracy without a fitting routine in the data handling computer. It is much easier to use the manufacturer's provision of differentation through a Savitzky–Golay cubic/quartic routine [12] and define the peak centre as the energy at which the differential is half-way between its two extrema. This is shown by point A in Fig. 2. Using a 1 eV differential, point A could be set to a precision of 5 meV. The shifts in energy of the volume plasmon and surface plasmon peaks as a function of temperature between 25 and 410° C are shown in Figs. 3a and b, respectively.

The feature at 9.9 eV is greatly enhanced at grazing

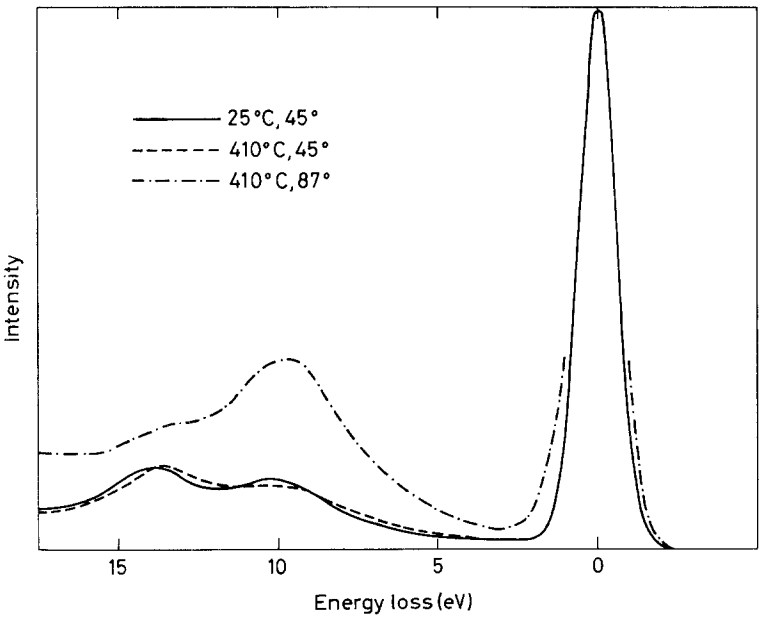

Figure 1 The plasmon losses for solid tin at 25° C and liquid tin at 410° C measured with the 1 keV electron beam at 45° and 87° to the surface normal.

incidence identifying it as a surface plasmon, whereas the feature at 14.0 eV is relatively unchanged, identifying it, in turn, as the bulk plasmon. These energies and identifications are broadly the same as those of Powell [13] and many others [14–16].

5. Discussion

For tin at 20° C, the density is given as 7300 kg m^{-3} [8]. Assuming there to be four valence electrons per atom, the bulk and surface plasmon energies may be calculated to be 14.29 and 10.11 eV, respectively, in close agreement with the experimental values. This indicates that the conduction electrons in tin behave as a free electron gas and that Equation 2 expressing the effects of dilation, may be expected to be valid. Equation 2 should thus be applicable to the thermal expansion in each phase. The solid lines in Figs. 3a and b show these dependencies and show that, indeed, Equation 2 is a very accurate description of the experimental data for the volume plamsons. Here the volume plasmon energies have been measured to a precision of 5 meV, allowing, in turn, temperatures of the micro-regions studied to be defined to $\pm 20°$ C.

The phase change occurring when tin melts at 232° C also involves a density change and hence a shift in the plasmon energy. The densities of tin just below and just above the melting point are 7191 and 7000 kg m^{-3}. This dilation causes a reduction in the volume plasmon energies of 0.19 eV which is easily measured and may consequently be used as an accurate temperature calibration point.

The data for the surface plasmon has less precision than that for the volume plasmon, as seen in Fig. 3b. The slope of the peak in the derivative is one third of that of the volume plasmon and so at low temperatures we see a scatter about three times that in Fig. 3a. Approaching the melting point we would expect changes in the microtopography which, in turn, affect the surface plasmon energy [4]. On melting, a small change in the shape of the surface plasmon peak occurs and its intensity relative to the volume plasmon falls by 10%. As the temperature is raised further, the surface plasmon weakens, relative to the volume plasmon, a further 23%. This change in the relative intensities leads to systematic uncertainties of the order of 50 meV in the position of the peak, even after

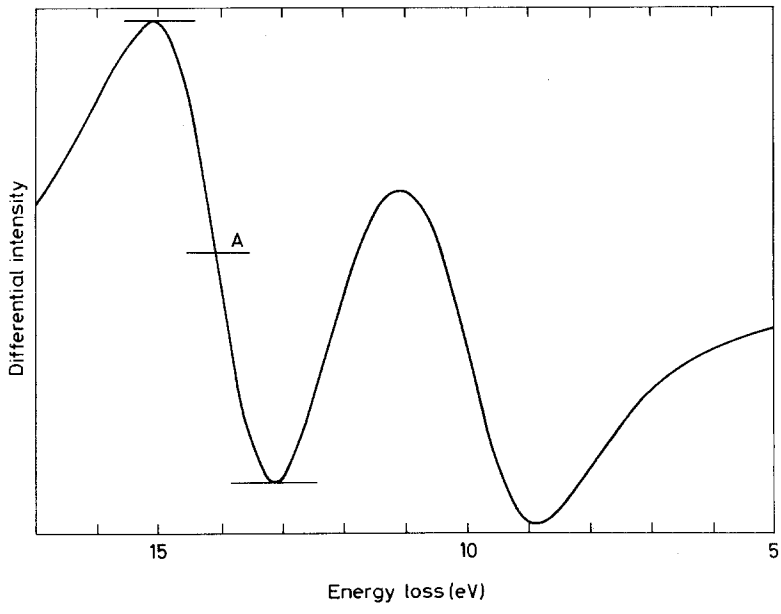

Figure 2 Differential of the plasmon peaks for tin at room temperature using a 21 point Savitzky–Golay quadratic/cubic differential smoothing function.

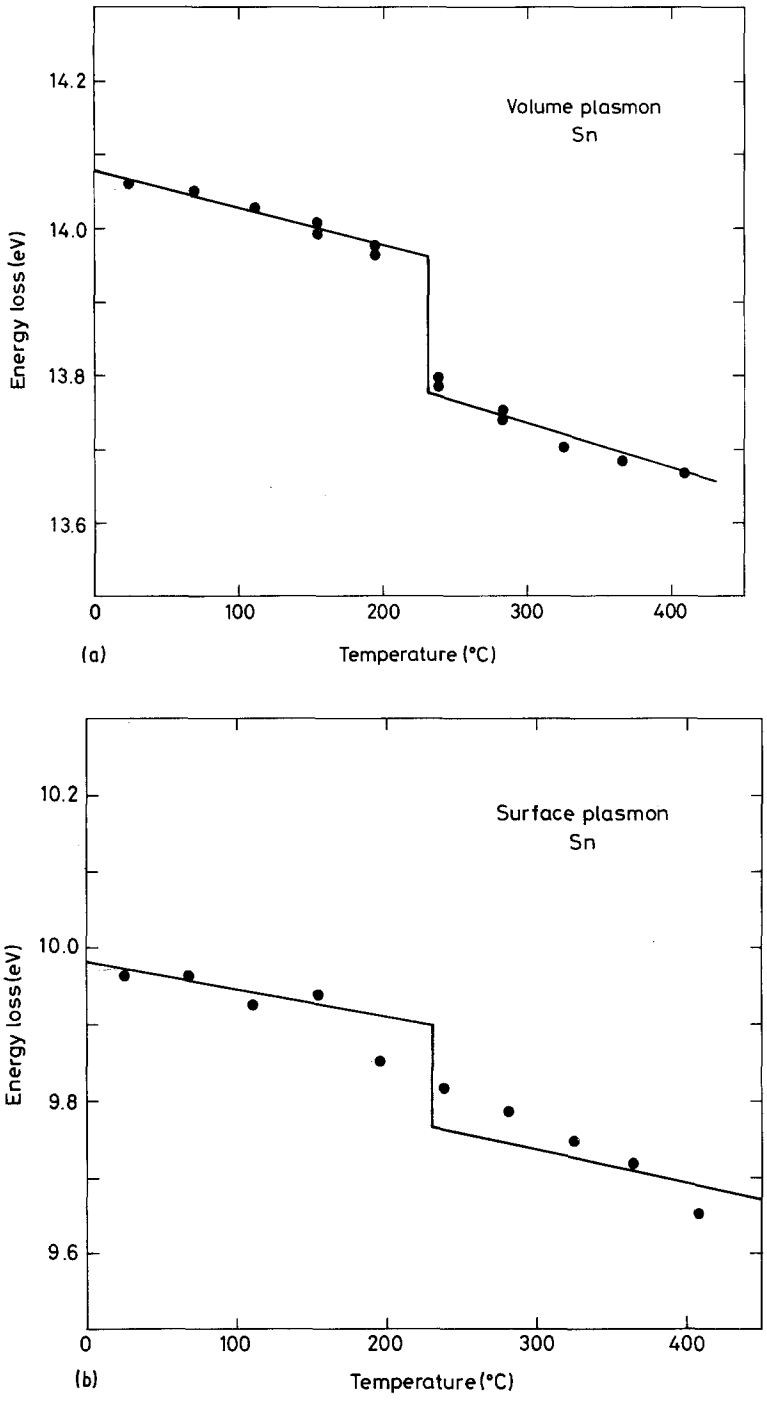

Figure 3 Measured loss energies, as a function of temperature, for the plasmons together with the predicted effect arising solely from density changes, (a) volume plasmons, (b) surface plasmons.

correction for the varying background slope from the volume plasmon. These effects may account for the difference between theory and experiment in Fig. 3b. Thus we see that the scatters discussed for the early work on temperature shifts [5, 6] may, only in some cases, be removed by an improved measurement capability.

We may summarize some of the points that should be noted in using the method. Since surface plasmons are sensitive to topographical changes they should be avoided and only the volume plasmons used. The calibration should be made using one analytical geometry and one electron beam energy since both the angular dispersion [17] and the momentum transfer [15] affect the plasmon energy observed. Additionally, for measurements of thin film devices on solid substrates, the temperature should not exceed that at which grain-boundary transport allows other elements to segregate to the free surface and so change its composition.

6. Conclusions

For tin a clear and easily understood shift of the volume plasmon energy occurs as a function of the sample temperature. The shift is directly related to either the reduction in density resulting from thermal expansion or that occuring as the solid melts. The shifts can be measured to better than ± 0.01 eV, leading to a temperature determination of ± 20 K that may be related to volumes considerably smaller than those relevant to VLSI circuits and may be achieved with thermal loads of less than 10 nW arising from the measurement method. In both reflection and transmission electron microscopy measurements the spatial resolution should be close to that of the normal imaging capability.

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