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Open system microthermometry – a technique for the measurement of local specimen temperature in the electron microscope

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For a sample in an open system (e.g. the vacuum of the electron microscope) the mass flux leaving the sample due to either sample evaporation, sublimation or thermal degradation will be uniquely controlled by the sample temperature. Classical kinetic theory shows that the mass flux rate depends on sample temperature and vapour pressure. By measuring the local rate of mass loss one can thus arrive directly at the local specimen temperature. Moreover, temperature-dependent kinetics of the phase change from the condensed phase to the vapour phase may be used to determine the local sample temperature over a continuous range of temperature due to heat input to the sample from the sample stage environment and the incident electron beam.

1. Introduction

Precise knowledge of the specimen temperature in the electron microscope is extremely useful but very difficult to determine. There have been relatively few direct measurements of the sample temperature [1–7] and these have generally employed either melting or a solid–solid phase transformation which limits knowledge of the sample temperature to be at or above (below) the particular fixed transition point temperature. Continuous temperature monitoring is, of course, possible by use of a thermocouple attached to the specimen holder at the specimen stage. The local sample temperature is, however, estimated by a single point calibration with a suitable phase change in the temperature region of interest.

The contribution to sample heating by the electron beam during sample observation and data collection will, however, not be detected by the thermocouple due to the large thermal inertia of the sample holder. Our concern is with the problems of continuous (in temperature and in time) local sample temperature measurement and with sample heating by the electron beam. In this paper we develop the general technique of open system microthermometry for the continuous measurement of local specimen temperature as determined by the heat input from the sample stage environment and electron beam. The technique is applied to the sublimation of ice particles for determination of the local sample temperature in a cold-stage environment.

2. Open system microthermomentry

For a sample in an open system (e.g. the vacuum of the electron microscope) the mass flux (in $\mathrm{kg\,m^{-2}\,sec^{-1}}$) leaving the sample due to either sample evaporation, sublimation or thermal

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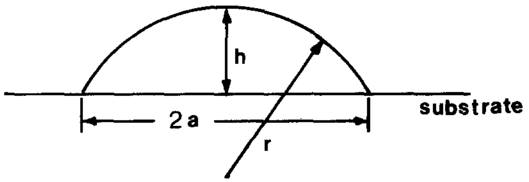

Figure 1 Schematic drawing of a spherical segment of height h, contact diameter $2a$ and radius r.

degradation will be uniquely controlled by the sample temperature. This is because the number of molecules leaving the condensed phase is a function of temperature only, whereas the number of molecules returning to the condensed phase depends on the partial pressure of the evaporating species in the surrounding atmosphere. For a typical microscope column vacuum of approximately 10^{-8} atm (essentially zero partial pressure), the mass loss rate is pressure independent. The mass flux, F, is given from classical kinetic theory by:

$$F = P_v(T)\left(\frac{M}{2\pi RT}\right)^{1/2} \tag{1}$$

where $P_v(T)$ is the vapour pressure at temperature T, M is the molecular weight, and R the gas contant.* By measuring the local rate of mass loss one can thus arrive directly at the local specimen temperature. This may be done by taking two successive micrographs of individual sample particles with a known time interval. Provided the particles are in good thermal contact with the substrate, their mass loss rate will yield the local (substrate) particle temperature. If, in addition the particle and substrate are heated by the incident electron beam, the increased mass loss rate will yield the temperature rise due to electron beam heating.

Fig. 1 is a schematic illustration of a spherical segment which we use to model a general particle shape. The spherical segment is of height h, contact diameter $2a$ and radius r. The particle volume V is:

$$V = 1/3\pi h^2(3r-h) \tag{2}$$

and if we assume a single component particle and that the mass loss rate is isotropic (e.g. $\mathrm{d}h/\mathrm{d}t = \mathrm{d}a/\mathrm{d}t$), then the rate of particle volume with time is just:

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \frac{\pi}{2}(a+h)^2\frac{\mathrm{d}a}{\mathrm{d}t}. \tag{3}$$

TABLE I

β	0	0.1	0.2	0.3	0.4	0.5
$\bar{\beta}$	0	0.38	0.69	0.88	0.98	1

The mass loss flux, F, is given by:

$$F = \frac{\rho}{S}\left(\frac{\mathrm{d}v}{\mathrm{d}t}\right), \tag{4}$$

where ρ is the particle density and S is the surface area. Since the particle "diameter" D is $2a$:

$$F = \frac{\rho[(D/2)+h]^2}{D^2+4h^2}\,\frac{\mathrm{d}D}{\mathrm{d}t}\,. \tag{5}$$

It is convenient to define a dimensionless geometrical parameter $\beta = h/D$ which serves to characterize the particle shape. F then becomes:

$$F = \frac{\rho(1+2\beta)^2}{4(1+4\beta^2)}\,\frac{\mathrm{d}D}{\mathrm{d}t} \tag{6}$$

which may be written

$$F = \frac{\rho}{4}(1+\bar{\beta})\,\frac{\mathrm{d}D}{\mathrm{d}t}\,, \tag{7}$$

where $\bar{\beta}$ is $4\beta/(1+4\beta^2)$. Table I shows that the mass loss flux is a relatively insensitive function of $\bar{\beta}$ (e.g. as β changes from 0 (a plate) to 0.5 (a hemisphere) F changes by only a factor of 2). As well, changes in F have a smaller effect on the determined temperature since large changes in the flux are caused by small temperature changes. Moreover, in a specific case, secondary electron imaging will provide an assessment for the choice of β. The sample temperature is then determined by choosing T (and hence $P_\mathrm{v}(T)$) so as to satisfy the following relationship (combining Equations 1 and 7) for the experimentally measured rate of change of particle diameter:

$$\frac{P_\mathrm{v}(T)}{T^{1/2}} = \frac{\rho}{4}(1+\bar{\beta})\left(\frac{2\pi R}{M}\right)^{1/2}\frac{\mathrm{d}D}{\mathrm{d}t}\,. \tag{8}$$

Therefore, we need an accurate knowledge of the vapour pressure–temperature relationship $P_\mathrm{v}(T)$ for the substance in question and that $P_\mathrm{v}(T)$ provide conveniently measured loss rate values in the region of interest (e.g. $0.01\ \mathrm{nm\,sec^{-1}} \leqslant \mathrm{d}D/\mathrm{d}t \leqslant 10\ \mathrm{nm\,sec^{-1}}$). Since we are interested in the steady state temperature $\mathrm{d}D/\mathrm{d}t$ will be given by $\Delta D/\Delta t$.

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* This assumes the coefficient of evaporation to be 1.0.

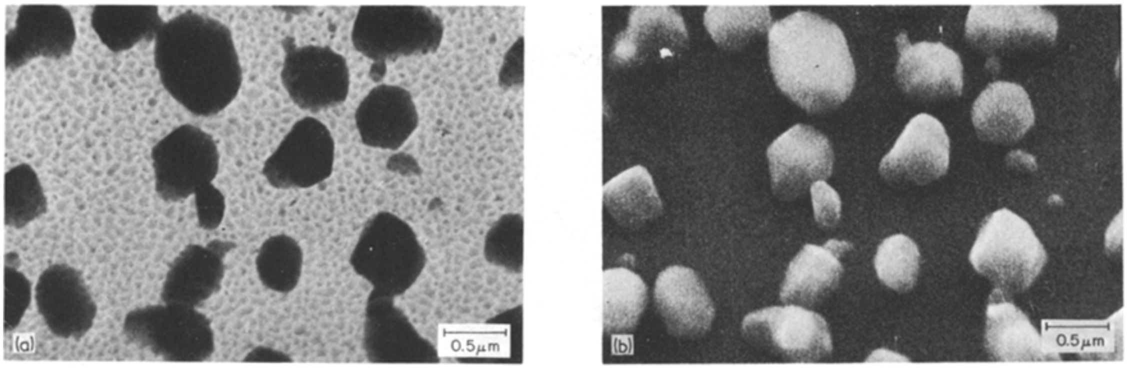

Figure 2(a) Scanning transmission electron micrograph of ice crystals on a thin polyimide membrane. Measured cold-stage temperature 93 K. (b) Secondary electron micrograph of ice crystals in (a) showing their polyhedral structure.

3. Application to cold stage microscopy

The vapour pressure–temperature relation for ice is quite accurately known to rather low temperatures [8]. The mass loss rates of individual ice crystals supported on a thin (~ 30 nm) polyimide membrane were studied at 100 keV in a JEOL JEM-100 CX STEM cold-stage equipped microscope. The thin polyimide film was cooled to 77 K in a liquid nitrogen bath and then exposed to ambient air for a few seconds in order to condense small ice crystals. The sample was then inserted in the cold stage of the microscope and experiments conducted using both liquid nitrogen and liquid Freon 1,4(CF_4) as coolants. The local intrinsic sample temperature was determined by obtaining low dose rate and low total dose micrographs taken at various intervals of time with the electron beam off between exposures. Current density values were taken from data made available by JEOL. We have previously calculated the expected sample temperature rise due to electron beam heating for various thickness samples and for a variety of electron-optical conditions [9–11]. These calculations show that sample beam heating should be completely negligible for the sample thicknesses and operating conditions used here. Radiation damage-induced mass loss by molecular displacement and/or radical migration after molecular dissociation, should also be negligible for the total doses employed [12, 13]. A copper–constantan thermocouple was used to monitor the cold-stage sample holder temperature.

Fig. 2 shows a secondary electron and transmitted electron image pair of a typical region of ice crystals. The crystals are approximately polyhedral with sizes from 10 to 100 nm. An appropriate value of β is ~ 0.5. The observed mass loss from ice crystals with liquid nitrogen as the cold-stage coolant was negligible over 5 to 10 min intervals in agreement with expected values. In order to observe reasonable particle dimensional changes in 5 to 10 min, Freon 1,4 which boils at 144 K was employed as the coolant. Successive STEM bright-field micrographs of an area were taken under minimum electron-beam heating and radiation damage conditions. The average of several "diameters" for each of several particles was used to determine F. For $\beta = 0.5$, the calculated value of the mass loss rate F is 2.7×10^{-7} $\text{kg m}^{-2}\,\text{sec}^{-1}$ corresponding to a local sample temperature of 163 K, a quite reasonable 10 K above the measured cold-stage temperature of 153 K.

The advantage of open system microthermometry is that the temperature-dependent kinetics of the phase change from the condensed phase to the vapour phase may be used to determine the local sample temperature over a continuous range of temperature due to heat input from the sample stage environment and the incident electron beam. Evaporation, sublimation or thermal degradation of the sample are equally good microthermometry processes and the choice of process and of substance depends only on the temperature range of interest.

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References

1. S. LEISEGANG, Proceedings of the 3rd International Conference on Electron Microscopy (London, Royal Microscopy Society 1954) p. 176.
2. J. VINE and P. A. EPSTEIN, *Proc. IEE* **111** (1964) 921.
3. L. REIMER and R. CHRISTENHUSZ, *Lab. Invest.* **14** (1965) 420.
4. G. J. ALMASI, J. BLAIR, R. E. OGILVIE and R. J. SCHWARTZ, *J. Appl. Phys.* **36** (1965) 1848.
5. J. M. SHORT, R. G. FERNQUIST and W. C. NIXON, IITRI/SEM/1976, Vol. 1 (1976) p. 45.
6. S. KRITZINGER and E. RONANDER, *J. Microscopy* **102** (1974) 117.
7. D. D. THORNBURG and C. M. WAYMAN, *Phys. Stat. Solidi.* **15** (1973) 449.
8. "International Critical Tables", edited by E. B. Washburn (McGraw Hill, New York, 1965) p. 21.
9. Y. TALMON and E. L. THOMAS, SEM, Proceedings of A Symposium, IITRI, Vol. 1 (1977) p. 265.
10. *Idem, J. Microscopy* **111** (1977) 151.
11. *Idem, ibid* **113** (1978) 268.
12. P. N. T. UNWIN and J. MUGURMA, *Phys. Stat. Sol.* **14** (1972) 207.
13. Y. TALMON, H. T. DAVIS, L. E. SCRIVEN and E. L. THOMAS, *J. Microscopy* (to be published).

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