A. POSSIBLE DESORPTION METHODS FOR MOLECULAR MICROSCOPY

Scanning desorption molecular microscopy is a method for studying surfaces by use of neutral molecules. The output is an image of the spatial variation of the interaction of neutral molecules with the specimen surface.\(^1\) For example, neutral molecules may be desorbed from a specimen surface by a scanning electron beam which heats the specimen surface locally and thereby desorbs neutral molecules.\(^2\) The desorbed molecules can be either a previously applied staining species (S), which bind preferentially to certain sites on the surface, or a species (I) that are intrinsic to the specimen.

Although in many cases the scanning electron-beam method appears to promise satisfactory performance, there are several potential problems. First, and this is particularly true for biological samples, some degree of electron radiation damage is to be expected. Second, in materials science applications, the desorption power requirement would be taxing, since metallic specimens seem to require four orders of magnitude more power than typical biological specimens. In view of these problems, several alternative desorption methods will be qualitatively described.

1. Chemical-Beam Desorption

In this method the following arrangement is envisioned (Fig. I-1). A beam of desorbing ions, \(D^+\), is focused and allowed to impinge on the specimen surface. (A neutral beam of D should also work, but would probably be more difficult to produce, focus, and scan.) Suppose that a staining species, S, has been previously applied to the surface. Then it is envisioned that D is selected so that a reaction

\[
D + S + \text{beam energy} \rightarrow X + V
\]

with a reasonable cross section exists, where V is some volatile reaction product, and

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X is either nonvolatile or nonexistent. If V is sufficiently volatile compared with S, V will be emitted wherever the beam \( D^+ \) or D impinges on a region where S resides. S, in turn, can be detected by a large solid-angle universal ionizer (U.I.). Although it may not be easy to find suitable reactions, the chemical-beam desorption method has the following advantages. Since heat generation is not required, this method may be useful in materials science applications where thermal desorption requires very high desorbing powers. Also, if a neutral beam of D can be used, there should be no radiation damage. Finally, this method may be directly applicable to a microscopic investigation of catalysis for which it offers a method of studying the spatial variations in function of a catalytic surface. It is emphasized that most methods of microscopy yield only structural information, whereas in this case both structural and functional information may be obtained.

2. Desorption from Below with an Electron Beam

The basic configuration planned for desorption molecular microscopy utilizes a scanning electron beam which impinges on the specimen from above, that is, from the side of the surface to be studied (Fig. I-2a). All electrons in the beam necessarily pass through the specimen surface, and therefore constitute a potential source of specimen radiation damage. Another possible configuration is shown in Fig. I-2b. In this case the electron beam impinges on a laminar specimen structure from below. For the three-layer structure shown as an example, the following behavior is expected: electrons from the beam pass through region 3 (low Z, high thermal conductivity; e.g., magnesium) with moderate energy loss and pass mainly into region 2 (high Z, poorer thermal conductivity; e.g., lead) where almost all of the energy is dissipated in a "bloom" volume. Only a few electrons reach region 1, the specimen, and the specimen surface to be studied is farthest removed from the source of electrons. Thus electron radiation damage should be greatly reduced compared with the case in which the
electron beam impinges from above.

Unlike the case of desorption from above, where a simplified calculation of the heat pulse shows that the desorbing temperature rise is very sharp in time and space, the "bloom" in Fig. I-2b is expected to generate only a gentle temperature rise at the specimen surface (qualitatively, curve T). The desorption rate, \( \dot{n} \), is a strong function of temperature, \( T \), through the approximate equation

\[
\dot{n} = \dot{n}_0 \exp(-E_0/kT),
\]

where \( n_0 \) is some attempt rate, \( E_0 \) is an activation energy, and \( k \) is Boltzmann's constant. Thus the spatial variation in desorption (qualitatively, curve D in Fig. I-2b) should be sharpened and nevertheless may give sufficient desorption contrast.

If it is necessary to prevent all electrons from reaching the specimen, additional thin layers can be provided between regions 1 and 2 so that a thin capacitor is formed. The potential drop across the capacitor can be made a few volts and of the correct sign, so that electrons are completely repelled from the specimen and radiation damage is avoided.

3. "Spark Chamber" Desorption

If the thin capacitor mentioned above has the correct properties, a very large quantity of heat may be produced by triggering a discharge of the capacitor (or driving the triggered discharge with an external source) by allowing high-energy electrons from a scanning electron beam to pass through the capacitor (Fig. I-3). To be suitable, an insulating material must be found which sustains sufficient damage in terms of ionized bonds to initiate the discharge. The material must also be sufficiently reversible in the
sense that, upon cessation of a rapid but moderate current, the discharge path will heal and recover to a high resistance. Also, the diameter, $d$, of the discharge region must not spread appreciably during the discharge time ($\sim 10^{-6} - 10^{-4}$ s). The advantages of this potential desorption method are large heat production with low radiation damage, since presumably only a few ($10^2$) high-energy electrons per minimum resolvable area may be needed to trigger a discharge.

Fig. 1-3.
Spark chamber desorption method.

In summary, several possible methods of desorption other than the straightforward exploitation of local heating by a conventional scanning electron beam have been described qualitatively in this report. Valuable discussions with J. G. King, M. G. R. Thomson and other members of the Molecular Beams Group are acknowleged.

J. C. Weaver

References

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