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Authors
Firment, L.E.
Somorjai, G. A.

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L. E. Firment and G. A. Somorjai

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LOW ENERGY ELECTRON DIFFRACTION (LEED) STUDIES OF MOLECULAR CRYSTALS:
THE SURFACE STRUCTURES OF VAPOR GROWN ICE AND NAPHTHALENE

L. E. Firment and G. A. Somorjai

Inorganic Materials Research Division, Lawrence Berkeley Laboratory
and Department of Chemistry; University of California,
Berkeley, California 94720

ABSTRACT

Low energy electron diffraction patterns have been obtained from
ice and naphthalene crystal surfaces vapor grown on the (111) face of
platinum at low temperatures. The surfaces of both molecular crystals
were well ordered, and can be identified as a hexagonal plane of ice
and the (001) face of naphthalene.
A very large group of materials, including most organic solids, can be classified as molecular crystals. Although their importance in surface science is widely recognized, they have not yet been studied by the various electron or atom scattering techniques that have been employed in recent years for investigating surfaces on the atomic scale. There have been no reports to date of the surface structure of molecular crystals by low energy electron diffraction (LEED). In this letter, we report the surface structures of two such materials: ice and naphthalene. We have grown crystals of each by vapor deposition, and have studied their surface morphologies as functions of substrate structure, temperature, and exposure. We have found that the crystals exhibit ordered surface structures when grown under the proper experimental conditions, and are fairly resistant to damage from electron bombardment.

The crystals were grown in a conventional LEED apparatus on a Pt(111) crystal surface. The platinum crystal was spot-welded to platinum bars attached to a hollow copper block. By flowing liquid nitrogen through the block and/or passing current through the platinum crystal, the platinum crystal could be held at any temperature between 100K and 1400K. The water and naphthalene vapors were introduced through a needle that permitted direct incidence of the molecules on the crystal surface, with fluxes in the range of $10^{13}$-$10^{15}$ molecules cm$^{-2}$sec$^{-1}$. The total pressure in the diffraction chamber could be maintained at $10^{-8}$ Torr by continuous ion pumping during the experiments.

The diffraction pattern shown in Fig. 1 was obtained by exposing the clean Pt(111) surface to water vapor flux of $10^{14}$ molecules cm$^{-2}$sec$^{-1}$, at substrate temperatures from 125-155K for several minutes. Below this
temperature range, the ice surface exhibited no diffraction pattern, indicating substantial disorder. Above this range, the Pt(111) diffraction features remained distinct, because the ice vapor pressure was too high for multilayer growth. The diffraction pattern has six-fold rotational symmetry, and it is almost identical to that expected from domains of a Pt(111)-(√3×√3) R30° surface structure, rotated 60° to each other. The pattern can be interpreted as from domains of the (111) face of the face centered cubic modification of ice (ice Ic), grown parallel to the Pt(111) surface, with the ice [110] parallel to the [1,1] or [1,1] of the platinum surface mesh. Alternatively, the pattern can be explained as due to the basal plane ([0001]) of hexagonal ice I, grown parallel to the Pt(111) surface, with the a direction ([100]) parallel to the [1,1] or [1,1] of the platinum surface mesh. The cubic form has been found to grow at these temperatures. Crystals with thicknesses up to 10^{-4} cm have been grown, as measured by optical interference techniques, and the surface order appeared to be independent of thickness.

Naphthalene chemisorbs readily on the Pt(111) surface at 300K, and the absorbed layer orders into a (6×6) surface structure up on heating the substrate to 400K. The best ordered naphthalene crystals were grown epitaxially on this (6×6) structure. With a naphthalene vapor flux of 10^{14} molecules cm^{-2} sec^{-1}, crystals exhibiting ordered surfaces could be grown between 105 and 200K. A disordered surface forms below this temperature range, and there is no multilayer growth above it. Multilayers of thickness similar to that of the ice were grown, and the diffraction pattern from the surface is shown in Fig. 2. The observed pattern is that expected from the monoclinic naphthalene crystals.
growing with their (001) plane (ab plane) parallel to the Pt(111) surface. The b direction ([010]) of each crystallite is parallel to one of the three [1,0] directions of the substrate surface mesh.

When naphthalene was deposited on the clean Pt(111) surface without first forming the ordered naphthalene monolayer structure, a ring-like diffraction pattern was observed. The radii of the concentric rings are equal to the distances from the specular beam to the previously described naphthalene diffraction spots. This indicates a naphthalene surface structure with the (001) plane again parallel to the substrate surface, but the naphthalene crystallites are rotationally disordered about the surface normal. Similar rotational disorder results when naphthalene is grown on a clean Pt(100) surface.

The effect of low energy electron bombardment (current density \( \sim 10^{-3} \text{ amp}\cdot\text{cm}^{-2} \)) on the surface structures of ice and naphthalene was also studied. The ice crystal surface remained ordered in the electron beam although excessive sublimation of water molecules seemed to occur. Using electron energies of about 100 eV, enough ice could be removed in minutes to allow the Pt(111) diffraction features to be observed. The naphthalene crystal surface was more sensitive to electron bombardment. At beam energies of about 30 eV, the diffraction pattern was obliterated within seconds, due to dis/ordering of the surface. Upon moving the electron beam along the surface, the diffraction pattern reappeared. It appears the electron beam induced disorder is localized to the area bombarded by electrons.
Secondary electron emission studies of ice and anthracene above 100 eV show that the flux of secondary electrons is greater than the incident flux, effectively removing negative surface charge. This is the likely reason for the relative ease of obtaining LEED patterns from the surface structures of these insulating molecular crystals. Below 30 eV a build-up of surface charge obliterates the diffraction features from both crystal surfaces. However, for layer thicknesses of less than $10^{-5}\text{Å}$, the diffraction patterns were detectable at all electron energies.

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REFERENCES

FIGURE CAPTIONS

Fig. 1. (a) LEED pattern of the ice surface at 74 eV. (b) Proposed surface structure of ice. The ice surface mesh is indicated by light lines, the Pt(111) surface unit cell is drawn with correct orientation at lower left. The oxygen atoms of the water molecules are indicated by dots, with the open dots lying above the plane of the filled dots. Dimensions shown for the ice lattice are bulk ice values.

Fig. 2. (a) LEED pattern of the naphthalene surface at 36.5 eV. The specular beam is left of center. (b) Schematic of the naphthalene LEED pattern, with specular beam position indicated, and one reciprocal unit cell drawn. Two other domains, rotated by 60° are also present. (c) Proposed surface structure of naphthalene with the Pt(111) surface unit cell drawn with correct orientation at lower left. Magnitudes of $\vec{a}$ and $\vec{b}$ vectors shown are those for bulk naphthalene.
Fig. 1b
Fig. 2a
Fig. 2b
Fig. 2c
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