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SECONDARY ION MASS SPECTROMETRY OF SMALL-MOLECULE SOLIDS AT CRYOGENIC
TEMPERATURES. V [1]. OXYGEN*

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ABSTRACT

Positive secondary ion mass spectra of neat solid O_2 and O_2 diluted with argon at 15-20K were measured as a function of the nature and energy of the primary ions (He^+ , Ar^+ , Kr^+ , 0.5-4.0 keV). With He^+ , the spectrum of solid O_2 is dominated by O_2^+ and O^+ peaks, with Ar^+ and Kr^+ , it is dominated by an intense cluster series O_{3n+2}^+ , $n = 0, 1, 2, \dots$.

INTRODUCTION

Low-temperature solids such as N_2 , NO , CO , N_2O , etc., yield intense series of clusters upon bombardment with heavy ions of keV energies [1-5]; similar results have been reported for solid ice [6], formic acid [7], acetone [8], and other materials. In many cases, the repeated solvating unit is identical with the molecule of the solid (e.g., N_2 , CO), but in some, it is different. For instance, the clusters obtained from solid NO have N_2O_3 as the repeated unit. In the present paper, we report our results for another simple solid, oxygen.

EXPERIMENTAL

The secondary ion mass spectrometer [2,4] and the experimental procedures [1] have been described elsewhere. Research grade extra dry oxygen gas was purchased from Matheson.

RESULTS

The positive secondary ion mass spectrum of solid O_2 is a strong function of the nature of the primary ion. With He^+ , the spectrum is weak and only the peaks for O_2^+ and, more weakly, O^+ , are observed. With Ar^+ and Xe^+ , the spectrum contains a peak at every multiple of 16, with the peaks corresponding to the compositions O_{3n+2}^+ far more intense than the others (Figure 1).

*Dedicated to Prof. R.M. MacFarlane on the occasion of his 50th birthday and presented at a symposium held in his honor at College Station, TX, USA, 15-18 May 1983.

The spectra of solid oxygen diluted with argon in various ratios were also measured. The positive SIMS of a 1:10 ($O_2:Ar$) mixture is shown in Figure 2.

Fig 1. Positive SIMS of solid oxygen.

Fig. 2. Positive SIMS of a solid oxygen-argon mixture (1:10).

DISCUSSION

The SIMS of solid oxygen is readily understood in terms of the mechanistic hypothesis formulated earlier [1,3,4,9]. With He^+ as the primary ion, only ions sputtered off the surface during the collision cascade phase early in the impact process are observed, with a broad energy distribution (O^+ , O_2^+). With heavier primary ions, the thermal spike region which subsequently develops has sufficient energy density to permit ejection of a large amount of material from the damage track into vacuum, producing slower cluster ions. The primary damage in the impact region will be due to the fragmentation, electronic excitation, and ionization due to fast nuclear motion and to secondary electrons:

Except for those species which are rapidly ejected during the collision cascade part of the event, the primary damage centers will be subjected to reactions with the excess O_2 present and possibly with each other, producing secondary damage centers. For instance, for neutral O atoms,

The charges will be scavenged by species of the lowest ionization potential or highest electron affinity: positive charge by O_2 , negative by O or O_2 . The positively charged clusters will probably still contain more O_2 than O_3 as they separate from the solid. As they cool off by loss of the least firmly bound constituents, they become enriched in the more polar and polarizable O_3 and yield the observed species: the most abundant $(\text{O}_3)_n\text{O}_2^+$ and the weaker $(\text{O}_2)(\text{O}_3)_n\text{O}_2^+$ and $(\text{O}_2)_2(\text{O}_3)_n\text{O}_2^+$.

The effect of dilution with argon also fits the proposed mechanism. More of the primary damage now involves argon atoms in processes such as

These defects are highly mobile and lead to secondary damage on oxygen in processes such as

Their high mobility is documented by the observation that O_2^+ is by far the most intense peak even in a 1:10 mixture and also appears as an intense

cluster series, Ar_nO_2^+ . Now, far less O_3 is available for the clusters, since the O atoms, formed in pairs, have much less opportunity to find an O_2 molecule to react with and either recombine or produce ArO^+ .

We conclude that the results obtained on solid O_2 agree with expectations based on the model proposed.

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