CRYSTALLIZATION OF THIN SELENIUM FILMS

S. A. Belan and I. E. Bolotov

UDC 536.421.4.1

The effect of the crystallization temperature and the substrate material on the morphology of the crystals produced by the heating of amorphous selenium films have been studied by electron microscopy and microscopic electron diffraction. The transition from ordinary crystallization to spherulite crystallization is found to be governed primarily by the crystallization temperature, and the spherulite crystallization is observed only at low temperatures. The substrate material affects only the ratio of the rates at which various crystal faces grow; it does not affect the transition from one type of crystallization to another. On all substrates, spherulites form as a result of the splitting of initial single-crystal nuclei; the crystallography of the splitting is the same.

There has recently been considerable interest in the study of the structure of thin films and the processes occurring in them for various kinds of preparation [1]. There is particular interest in crystallization in thin films of amorphous selenium because spherulites—a common type of crystal, whose formation mechanism has not been adequately studied—often form during annealing [2]. Such films are formed during the vacuum condensation of selenium onto a substrate at room temperature.

Depending on the crystallization conditions, the crystal nuclei in a given substance may form either spherulites or single crystals. Here the morphology and crystal texture of the spherulites themselves depend on the crystallization conditions; in different cases, the result may be either positive spherulites, negative spherulites, or spherulites displaying no birefringence [3].

Since no systematic information is available about the effects of various crystallization parameters on the structure of spherulites or on the transitions from spherulite crystallization to ordinary crystallization, we have carried out a corresponding study; we report here a study of the effect of crystallization temperature and substrate material on spherulite formation in thin selenium films.

1. Experimental

The spherulite nuclei were studied by electron microscopy and microscopic electron diffraction. The substrates studied can be divided into two classes: crystalline (mica and NaCl) and amorphous (carbon, germanium, and quartz).

The amorphous selenium films of the order of 1000 Å in thickness were produced by vacuum condensation of selenium by the procedure described in [4]. Crystalline nuclei forming in the temperature range 100 to 160°C were studied.

2. Crystallization on Amorphous Substrates

The crystalline nuclei which form at 160°C on amorphous substrates are regular single crystals having the shape of very elongated rhombuses (Fig. 1). The c-axis of the hexagonal selenium cell coincides with the minor diagonal of the rhombus, as is shown by microscopic electron diffraction patterns obtained from individual crystals.

With an increase in the annealing time, the rhombic nuclei increase in size, remaining regular single crystals. Only in some of the crystals can one observe a splitting of the acute angle and the formation of two or more filaments.


© 1972 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for $15.00.
The crystallization at 100°C occurs in a different manner. In this case the smallest nuclei which can be observed are finger-shaped crystals, slightly broadened at the ends and having a filamentary structure (Fig. 2a). The electron diffraction patterns of such nuclei show that the c-axis lies within the plane of the film and perpendicular to the crystal length. Here the film plane coincides with one of the [0001] prismatic planes of the second kind. The diffraction pattern reflections are slightly blurred into arcs, even for the smallest crystals. This blurring results from the fact that even the small crystals are slightly sheaflike (they are slightly broadened at the ends). During subsequent growth, this broadening increases, and these nuclei convert into split sheaflike crystals consisting of diverging filaments (Fig. 2b).

Microdiffraction studies of various parts of a single sheaflike crystal show that the c-axis in each region is initially perpendicular to the filament direction in this region. Here the c-axis lies in the plane of the film as before. Accordingly, a crystal is produced having a spherulite texture – the c-axis is more or less concentric. As the growth proceeds, however, the crystal lattice usually rotates in such a manner that the