THE STRUCTURE OF SELENIUM

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Electron diffraction investigations of layers of hexagonal Se deposited in vacuum have revealed [1] that the structure and orientation of the crystals depend to a considerable extent on metallic impurities (In, Tl). The presence of these impurities causes the small crystals of selenium to be aligned with the basal plane parallel to the backing (the texture axis is [0001]) instead of having the usual orientation with the face ($10\bar{1}0$) parallel to the backing, which is caused by the presence in the Se structure of spiral-shaped atomic chains, aligned with their axes in the plane of the backing.

The structure of hexagonal selenium was first studied in an x-ray investigation by Bradley [2]: a = 4.35, c = 4.95 Å, c/a = 1.14, and space group D_3^4. The only coordinate parameter for Se atoms, x = 0.21, was determined to within 0.01. In this investigation, we made a more precise determination of the coordinate of the Se atoms and studied the influence of impurities, in particular Pd, on the crystallization and orientation of Se films.

The samples for the electron-diffraction investigations were prepared in the form of thin films by sublimation in a vacuum either of pure selenium, or by sublimation of individual vaporizers of selenium and palladium. In the case of vaporization of pure selenium on a freshly cleaved surface of NaCl with subsequent annealing at a temperature of 200°C for a period of 3-4 h we obtained electron-diffraction patterns of the type shown in Fig. 1. The small Se crystals were oriented with the face ($10\bar{1}0$) parallel to the backing. In this case the small crystals develop in the form of long hexagonal prisms, the pronounced development of prismatic faces leading, despite the acicular habit, to the formation of texture. The geometry of such electron-diffraction patterns is interpreted in [3]. The parameters of the unit cell of Se were determined from the electron-diffraction patterns: a = 4.30, c = 4.89 Å; c/a = 1.14. It should be emphasized that the values of the parameters a and c are somewhat lower than the values given by Bradley [2]. About 95 reflections were recorded in the electron-diffraction patterns. In order to make a more precise determination of the structure of the hexagonal phase of Se, we determined the experimental intensities of the reflections, the hk0 reflections being measured microphotometrically and used as blackening marks in a visual estimate of the remaining reflections. The equation of the kinematic theory was used for the transition from the intensities to the structure amplitudes. Since $\Phi_{hkl}^{theor} \neq \Phi_{khl}^{theor}$ for the structure factors, but the hk$l$ and kh$l$ reflections coalesced in the electron-diffraction patterns, their intensities were determined according to the ratio of the squares of the theoretical structure amplitudes. The R factor was minimized in order to determine the parameter x more accurately. The minimum value of the R factor, namely 13.6%, was obtained with x = 0.218 ± 0.003 and a value of the temperature factor of B =

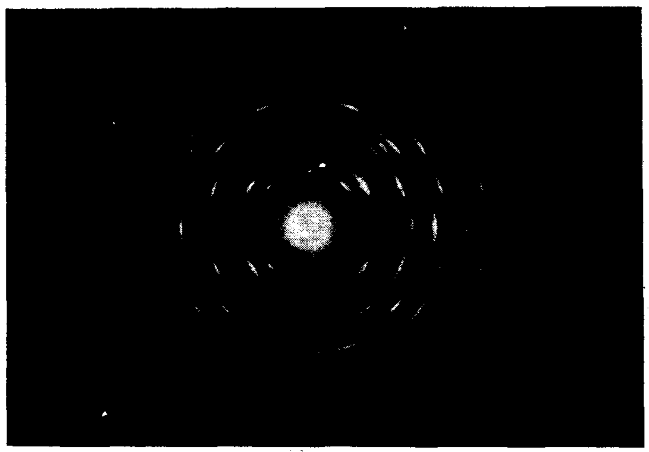

Fig. 1. Electron-diffraction pattern from selenium; the texture axis is [1010].

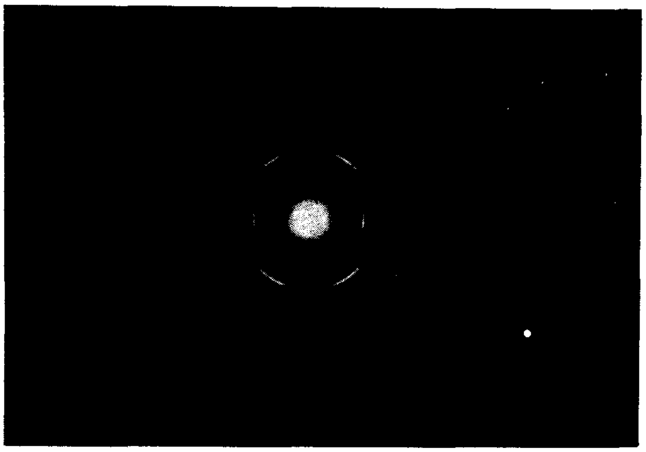

Fig. 2. Electron-diffraction pattern from selenium; the texture axis is [0001].

0.3, the distance between the Se atoms in the chain being equal to 2.31 Å.

In order to investigate the influence of the impurity Pd on the Se structure, we prepared films by simultaneous vacuum sublimation of Se and Pd from different vaporizers. Different alloys of Se with Pd were formed on the sodium chloride crystals, onto which the films were vaporized; in this case, the crystals were placed close to the palladium vaporizer. Amorphous Se films with a small amount of the impurity Pd were formed under the selenium vaporizer; after a short period of annealing (at t = 120°C for a period of 1-2 h) these films were transformed into a textured film of hexagonal selenium with the orientation [0001] (Fig. 2). The cause of the formation of crystals of such habit and the acceleration of the crystallization process was the presence of the impurity Pd, which served to break the spiral chains of selenium atoms [1].

LITERATURE CITED

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