Journal of Alloys and Compounds 434–435 (2007) 275–278

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Peculiar crystallization of amorphous selenium in the presence of organic liquids: Effects of addition of titanium oxides

Kazuaki Ikeda*, Tsukio Ohtani

Laboratory for Solid State Chemistry, Okayama University of Science, Ridai-cho 1-1, Okayama 700-0005, Japan

Abstract

We have previously observed that amorphous Se crystallized into hexagonal Se or α-monoclinic Se, when exposed to various organic fluids at room temperature. Here we report the effects of coexistence of TiO_2 (rutile and anatase) on the crystallization of amorphous Se in various organic liquids (acetone, methanol and benzene). It was found that the presence of TiO_2 has a tendency to promote formation of hexagonal Se crystals under light, which is interpreted in terms of photocatalytic effects of TiO_2 inducing local electrostatic field around the Se particles.

Keywords: Amorphous selenium; Hexagonal selenium; Monoclinic selenium; Crystallization of Se; Photocatalytic effect

1. Introduction

Elemental selenium is used in many applications: photocells, xerography, solid-state image sensors, etc. The common phases are hexagonal Se (*h*-Se) [1], α-monoclinic Se (α-*m*-Se) [2], β-monoclinic Se (β-*m*-Se) [3], and amorphous Se (*a*-Se) [4,5]. The *h*-Se is obtained by slowly cooling molten Se [1], the α-*m*-Se and the β-*m*-Se by evaporation from CS_2 solution [2,3], and *a*-Se by quenching from high temperatures [4,5]. In addition to the common phases, Se has some other polytypes: γ-monoclinic [6], rhombohedral [7], orthorhombic [8], etc. The *h*-Se is thermodynamically the most stable one. All the others are metastable, being converted to the *h*-Se by warming. The *a*-Se is an ordinary commercial form, and is now widely used in photoconversion layer of solid-state image sensors such as highly sensitive camera tube [9]. All phases of Se are scarcely dissolved in most organic liquids at room temperature. Fig. 1 shows schematic crystal structures of the *h*-Se and the α-*m*-Se. The *h*-Se crystal consists of parallel infinite chains of Se, where the Se atoms are arranged in helical spirals along the crystalline *c* axis [1]. All the monoclinic phases are molecular crystals, being composed of building blocks of Se_8 molecules arranged in a crown shape; they are different with each other only in packing mode of the molecules [2,3,6]. The structure of the *a*-Se is basically built from disordered helix-like Se chains with minor contribution of Se_8 rings [10].

More than 100 years ago, Saunders found the phase change from *a*-Se to *h*-Se or to monoclinic Se in contact with various organic liquids at ordinary temperatures [11]. Saunders, however, gave no suggestion on the origin of these phenomena. Recently, we have newly found that the *h*-Se crystals with fibrous or needle like morphology were grown in the liquids with higher dielectric constant such as acetone and pyridine (relative dielectric constant ε_r is higher than 4.0), and polyhedral crystals of α-*m*-Se were formed in the liquids with lower dielectric constant such as benzene and hexane (ε_r is less than 2.4) [12]. The noticeable is that the grown phase is dependent of the chirality of camphor: *h*-Se and α-*m*-Se crystals formed under the vapor of *d*- and *l*-camphor, respectively. We concluded that the crystallization is not caused by the precipitation from the solution, but by a catalytic mechanism of organic molecules adsorbed on the surfaces of *a*-Se particles.

In the present study we carried out further investigation to reveal the origin of these curious phenomena, by adding TiO_2 (rutile and anatase) to the organic liquids + *a*-Se systems. Since titanium oxides are widely used as photocatalysts [13], we expected that the reactions are influenced by the light irradiation in the presence of these oxides.

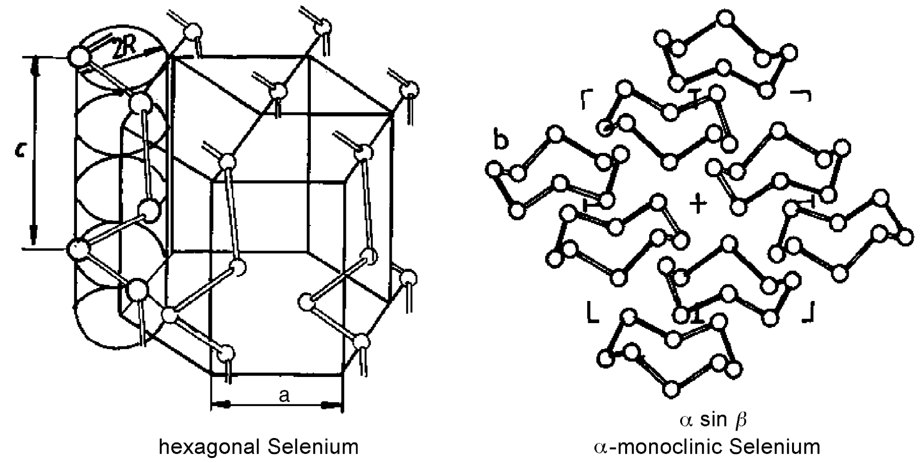
2. Experimental

Commercial amorphous Se (*a*-Se) shots (99.9999% in purity: Rare Metallic Co., Ltd.) were ground into powder form by using an agate mortar. The *a*-Se

---

* Corresponding author.
E-mail address: s98c006@mail.chem.ous.ac.jp (K. Ikeda).

0925-8388/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2006.08.248



hexagonal Selenium

α-monoclinic Selenium

Fig. 1. Crystal structures of the hexagonal Se phase and the α-monoclinic Se phase.

powder of about 0.3 g and TiO_2 (rutile and anatase) of 0.1 g was put into organic liquid (acetone, methanol or benzene) of about 1 ml contained in a silica glass capsule, and then was kept still at room temperature under visible light for 30 days. Samples after the reaction were analyzed by X-ray diffraction (XRD) technique and by scanning electron microscopy (SEM) observation.

3. Results and discussion

Fig. 2 shows XRD patterns of the Se samples after the reaction in acetone for 30 days at room temperature under the visible light in the presence of no oxide, rutile and anatase. When *a*-Se was exposed to acetone (no oxides), the *a*-Se was almost entirely transformed into *h*-Se crystals. The *h*-Se phase also was formed when rutile or anatase was coexisting. Fig. 3 exhibits XRD patterns of the Se samples, when the *a*-Se was exposed to methanol under the visible light in the presence of no oxide, rutile and anatase. In the absence of oxides the *a*-Se was transformed into the *h*-Se crystals together with a small amount of α-*m*-Se crystals. When rutile was added, the *a*-Se was changed into the α-*m*-Se phase, while the *h*-Se phase was formed in the presence

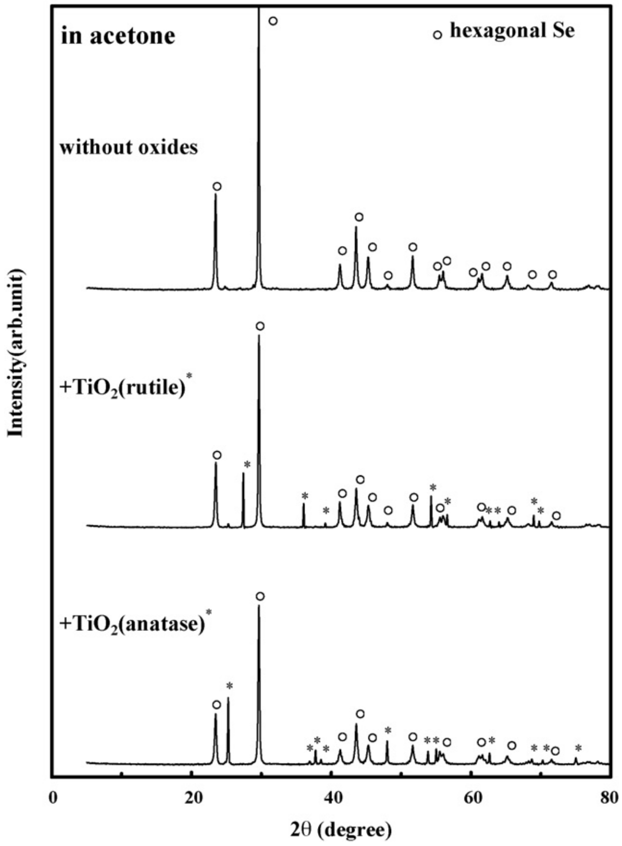


Fig. 2. XRD patterns of the Se samples after the reaction in acetone for 30 days at room temperature under the visible light in the presence of no oxide, rutile and anatase.

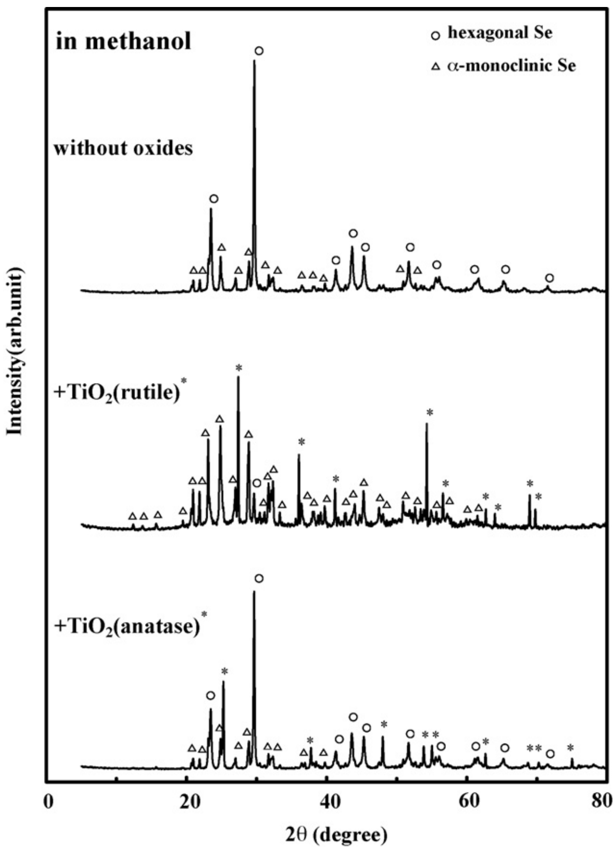


Fig. 3. XRD patterns of the Se samples, when the amorphous Se was exposed to methanol under the visible light in the presence of no oxide, rutile and anatase.

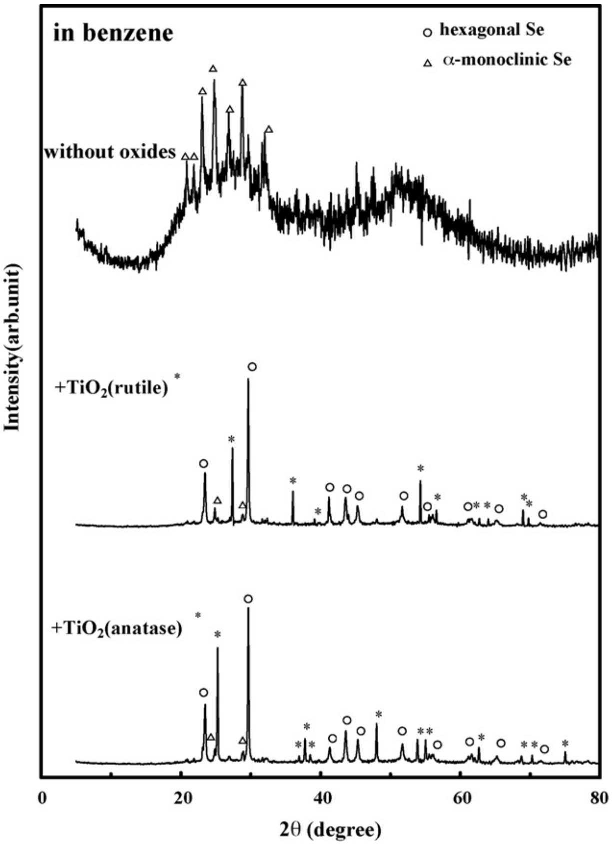


Fig. 4. XRD patterns of the Se samples reacted in benzene under the visible light in the presence of no oxide, rutile and anatase.

of anatase. Fig. 4 shows XRD patterns of the Se samples reacted in benzene under the visible light in the presence of no oxide, rutile and anatase. In the absence of oxides the *a*-Se was changed into α-*m*-Se. In the presence of rutile or anatase the *h*-Se phase was predominantly formed.

The obtained results are summarized in Table 1, where only the predominantly produced phases are shown for each case. In our previous paper, we considered that organic molecules adsorbed on the *a*-Se surfaces may act as a catalyst on the crystallization of *a*-Se [12]. The present results appear to show that the coexisting titanium oxides also play a catalytic role on the reactions. The effects of the addition of titanium oxides were observed most significantly in the reactions of the benzene + oxides system under the visible light. By exposing the *a*-Se to benzene (no oxide), the *a*-Se was converted into the α-*m*-Se phase, which is possibly due to the low dielectric constant of benzene ($\varepsilon_r = 2.274$ [14]). On the other hand, the addition of titanium oxides produced nearly the single phase of *h*-Se under the light. We have already observed that the *h*-Se crystals were grown in the organic liquids with relatively high dielectric constants such as acetone ($\varepsilon_r = 20.7$ [14]) and methanol ($\varepsilon_r = 32.66$ [14]). This may lead to the consideration that the electrostatic field around the Se particles may be responsible for the formation of the *h*-Se phase. The present titanium oxides are well known photocatalysts, which may induce the local electrostatic field around the *a*-Se particles under the light. Thus, the photocatalytic effects would have an important role for the formation of the *h*-Se phase. In order to see the light irradiation effect, we performed the reaction of benzene + TiO$_2$ (rutile and anatase) systems in the absence of light for 30 days, and found that the *a*-Se did not react into the *h*-Se phase, but into the α-*m*-Se phase. These results mean that the electrostatic field locally induced by the photocatalytic mechanism is surely an important key factor for the formation of the *h*-Se phase. The role of the electrostatic field for the formation of the *h*-Se phase would be related to that the *h*-Se crystals possess the relatively higher dielectric constant along the *c* axis ($\varepsilon_r = 10–13$) compared to that of the α-*m*-Se crystals ($\varepsilon_r = 6–7$) [15]. The formation of the α-*m*-Se phase in methanol + rutile system under the visible light may not be simply interpreted by the photocataysis mechanism. But, the *h*-Se phase was obtained in this system under ultraviolet (UV) radiation, indicating that the photocatalitic effect was enhanced

Table 1
Se phases predominantly produced in the organic liquids + TiO$_2$ system under the visible light irradiation

Organic liquids	No addition	+TiO$_2$ (rutile)	+TiO$_2$ (anatase)
Acetone	*h*-Se	*h*-Se	*h*-Se
Methanol	*h*-Se	α-*m*-Se	*h*-Se
Benzene	α-*m*-Se	*h*-Se	*h*-Se

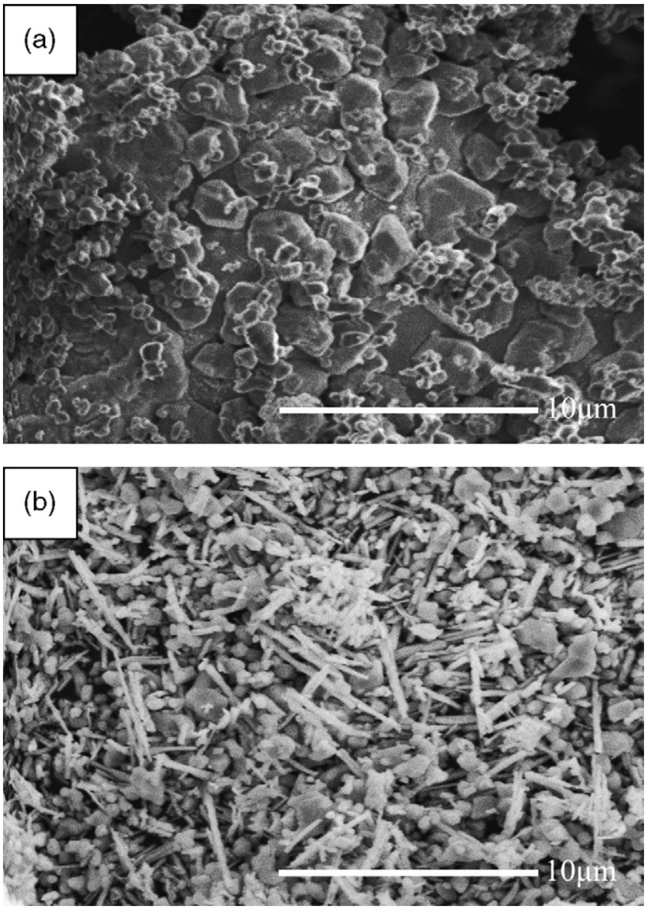


Fig. 5. SEM images of the Se crystals formed in methanol in the presence of rutile at room temperature for 30 days: the α-*m*-Se crystals obtained under the visible light (a), and the *h*-Se crystals obtained under the ultraviolet radiation (b).

by the UV irradiation. Fig. 5 gives SEM images of the Se crystals formed in methanol in the presence of rutile at room temperature for 30 days: the α-*m*-Se crystals obtained under the visible light (Fig. 5(a)), and the *h*-Se crystals obtained under the ultraviolet radiation (Fig. 5(b)). The α-*m*-Se crystals have the many-faced polyhedral morphology, and those of the *h*-Se crystals the stick or needle morphology. Small irregular particles are the coexisting rutile. These morphologies of the Se crystals are identical to those observed in the previous work [12].

4. Conclusions

The amorphous Se (*a*-Se) in benzene liquid was changed into the hexagonal Se (*h*-Se) crystals in contact with TiO_2 (rutile and anatase) under the visible light, while the α-monoclinic Se (α-*m*-Se) crystals was formed in the absence of light. The *h*-Se crystals were grown in acetone liquid in the presence of rutile and anatase, and were formed in methanol in contact with anatase under the visible light. In methanol liquid the α-*m*-Se crystals were predominantly grown in the presence of rutile under the visible light, but changed into the *h*-Se crystals under ultraviolet radiation. These results were interpreted in terms of the photocatalytic effects of TiO_2, inducing the local electrostatic field around the *a*-Se particles. These phenomena will lead to new applications such as chemical sensors, and will open the way to study novel catalytic reactions.

Acknowledgment

This work was supported in part by “High-Tech Research Center” Project for Private Universities.

References

[1] P. Cherin, P. Unger, Inorg. Chem. 6 (1967) 1589.

[2] P. Cherin, P. Unger, Acta Crystallogr. B28 (1972) 313.

[3] R.E. Marsh, L. Pauling, J.D. McCullough, Acta Crystallogr. 6 (1953) 71.

[4] E.H. Henninger, R.C. Buschert, L. Heaton, J. Chem. Phys. 46 (1967) 586.

[5] H.Z. Krebs, Anorg. Allg. Chem. 265 (1951) 156.

[6] O. Foss, V. Janickis, J. Chem. Soc. Dalton Trans. 4 (1980) 624.

[7] Y. Miyamoto, Jpn. J. Appl. Phys. 19 (1980) 1813.

[8] K. Nagata, H. Tashiro, Y. Miyamoto, Jpn. J. Appl. Phys. 20 (1981) 2265.

[9] Y. Takiguchi, H. Maruyama, M. Kosugi, F. Andoh, T. Kato, K. Tanioka, J. Yamazaki, K. Tsuji, T. Kawamura, IEEE Trans. Electron. Devices 44 (1997) 1783.

[10] M.A. Popescu, Non-Crystalline Chalcogenides, Kluwer Academic Publishers, Dordrecht/Boston/London, 2000.

[11] A.P. Saunders, J. Phys. Chem. 4 (1900) 423.

[12] T. Ohtani, N. Takayama, K. Ikeda, M. Araki, Chem. Lett. 33 (2004) 100.

[13] A. Fujishima, K. Honda, Nature 238 (1972) 37.

[14] D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics, 74th ed., CRC Press, Inc., Boca Raton, Ann Arbor, London/Tokyo, 1994.

[15] O. Madelung (Ed.), Landolt-Bornstein (New Series), vol. 17, Springer-Verlag, Berlin/Heidelberg, 1983, p. 86.