CsI(Tl) films: deposition, examination of structure and scintillation

A.Lebedinsky, A.Fedorov, A.Ananenko, P.Mateychenko

Scientific and Technologic Corporation "Institute for Single Crystals",
National Academy of Sciences of Ukraine,
60 Lenin Ave., 61001, Kharkiv, Ukraine

The sublimation of the bulk CsI crystal with optimal activator concentration instead of powder source use at vacuum deposition of CsI(Tl) films has been shown to provide CsI(Tl) films with required content and uniform distribution of activator in the film volume. The CsI(Tl) films produced by this technology demonstrate superior scintillation characteristics in comparison with CsI(Tl) films deposited by a usual technology. The dependence of the film crystalline structure on the deposition conditions has been studied in detail.

Показано, что применение сублимации монокристалла CsI(Tl) с оптимальной концентрацией активатора вместо порошкового источника при вакуумной конденсации пленок CsI(Tl) позволяет получить пленки CsI(Tl) с необходимой концентрацией и однородным распределением активатора в объеме пленки. Пленки CsI(Tl), полученные с применением такой технологии, демонстрируют сцинтилляционные параметры, превосходящие параметры пленок CsI(Tl), полученных по общепринятой технологии. Подробно исследована зависимость кристаллической структуры пленок от условий осаждения.

CsI(Tl) films produced by vacuum deposition are used now as scintillation medium for image forming devices in X-ray or γ-radiation. The application of CsI(Tl) films in those devices is justified by its high light yield and short scintillation decay time. Moreover, the CsI(Tl) emission spectrum matches well with photon sensitivity of amorphous silicon detector arrays (a-Si:H) [1, 2]. Due to the trend of CsI(Tl) films produced by vacuum deposition to grow in columnar morphology, these films possess increased spatial resolution. The reason is that the separate CsI(Tl) columns act as light guides, suppressing the lateral light scattering due to the total internal reflection on the column boundaries [3].

The proper activator content and uniform activator distribution play a key role for high scintillation efficiency of CsI(Tl) films. To achieve the required activator content and distribution in the films at vacuum deposition, evaporation from two powder sources containing CsI and some thallium compounds is often used [2]. Another way is the dopant diffusion to CsI from an additionally deposited TlI layer under annealing [4]. An alternative way to produce CsI(Tl) films with required activator content and uniform distribution without evaporation from two sources or annealing is proposed in this work. Moreover, the crystalline structure and scintillation properties of CsI(Tl) films obtained by vacuum deposition are discussed.

The CsI(Tl) scintillator films were produced by physical vapour deposition (PVD) technique in a vacuum better than $5 \cdot 10^{-3}$ Pa from CsI source with 0.1 wt.% Tl. The CsI(Tl) films were deposited onto two substrate types. The first type, the (100) cleavage plane of LiF single crystal, was used as an orienting substrate while the second one, glass, was employed as an amorphous non-orienting substrate. The substrate and crucible temperatures were controlled by computer-driven interface that provided the assigned deposition rate and substrate temperature during the whole deposition process. The substrate temperature varied
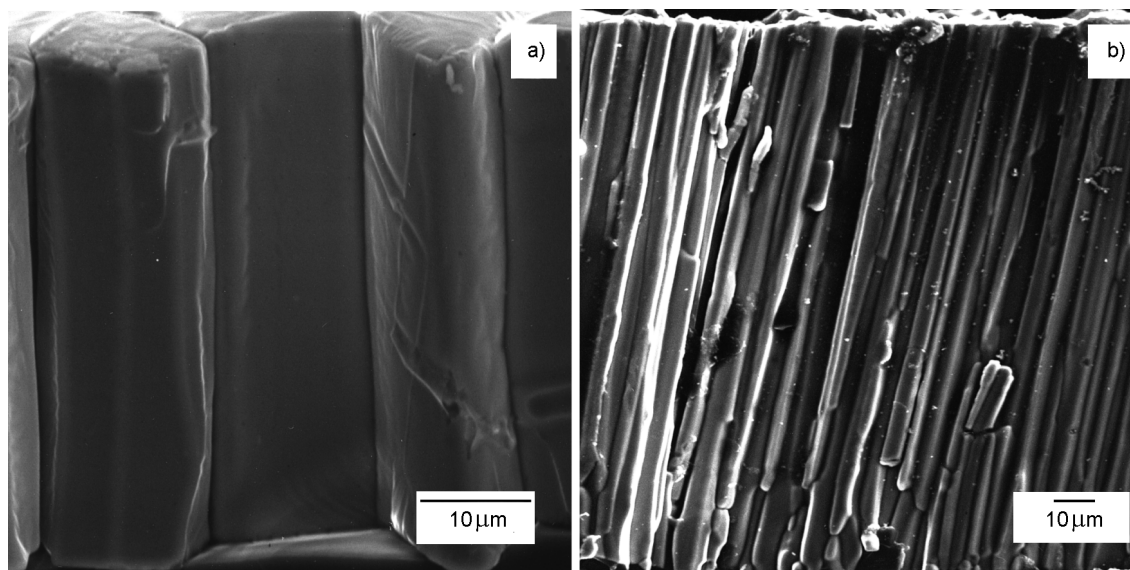
Fig. 1. SEM images of CsI(Tl) films cross section: a) CsI(Tl)/(100) cleavage plane of LiF single crystal, b) CsI(Tl)/glass.

from 373 K to 573 K. The deposition rate was measured using a previously calibrated quartz oscillator placed near the substrate holder; it was from 1 $\mathring{A}$/s to several hundreds $\mathring{A}$/s. The film crystalline structure was examined by X-ray diffraction in Cu K$_\alpha$ radiation using diffractometer with a graphite monochromator in the primary beam. In the case of single crystalline layer blocks, their structure perfectness was estimated by X-ray rocking curves obtained by a double crystal X-ray spectrometer with a Si monochromator adjusted to (400) reflection of Cu K$_{\alpha 1}$ radiation. The cross section images of samples were obtained by a JSM 820 scanning electron microscope. Scintillation processes in the samples were excited by 5.15 MeV α irradiation from ^{239}Pu source. The CsI(Tl) film pulse height spectra were obtained using a Hamamatsu 1307 photomultiplier connected to the multichannel amplitude analyzer AMA-03F.

The deposition of CsI(Tl) films by PVD results in columnar morphology of the growing layers. Moreover, the columnar morphology of CsI(Tl) films appears regardless of the substrate type (Fig. 1). The previously published results [5] show that CsI(Tl) films produced by PVD usually possess a polycrystalline structure. In this work, the relationship between the deposition conditions and the film structure has been examined in detail. It is well known that the substrate temperature (T_s) should be no less than two thirds of melting point (T_m) of the material being condensed for

good adatom mobility that, in turn, defines the growing layer structure. So, the substrate temperature was chosen to be 573 K, since the CsI melting point is 933 K. At this substrate temperature and low deposition rate (below 10 $\mathring{A}$/s), the CsI(Tl) condensation onto (100) LiF single crystal substrate provides the single crystalline structure of the film column blocks. X-ray diffraction shows that CsI(Tl) films obtained at these conditions have two preferred orientations, namely, [110] and [112], in contrast to the [100] substrate orientation (Fig. 2a). To confirm the single crystalline structure of reflecting blocks, X-ray rocking curves were obtained. The half-widths of reflections were in the range from 10 to 24 arc minutes for (110) reflections and from 6 to 23 arc minutes for (112) reflections. These halfwidth values can be compared with 2 arc minutes halfwidth of the (200) LiF substrate reflection, consequently, it was concluded that CsI(Tl) films deposited under these conditions possess adequate crystalline perfection. However, at the same substrate temperature 573 K, the deposition rate increasing up to tens $\mathring{A}$/s leads to deterioration of the film crystal perfection. This follows from immeasurable values of the rocking curve halfwidth and appearance of new reflections from other crystallographic planes (Fig. 2b). In these conditions, the well-defined film texture with (110) and (112) preferred orientations is observed (Fig. 2b). So, the preferred film orientations are retained but the single crystalline structure disappears. At decreased substrate
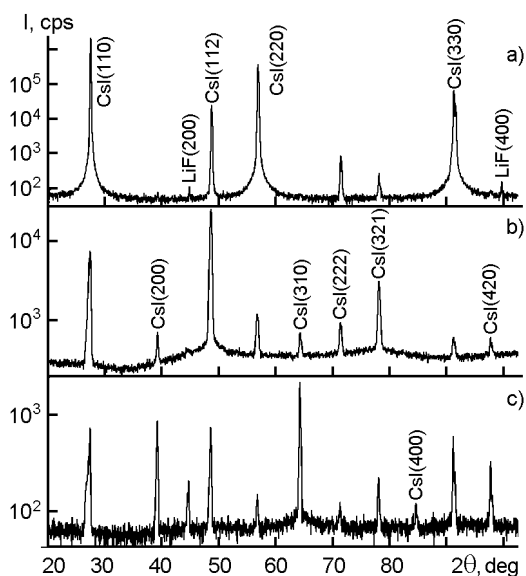
Fig. 2. X-ray diffraction patterns of the CsI(Tl) films deposited onto LiF (100): a) deposition rate 3 Å/s, substrate temperature 573 K; b) deposition rate 45Å/s, substrate temperature 573 K; c) deposition rate 120 Å/s, substrate temperature 443 K.

temperature (423 K) and deposition rate increased to hundreds Å/s, the CsI(Tl) films possess typical polycrystalline structure without any preferred orientations (Fig. 2c).

The obtained morphology of CsI(Tl) layers (Fig. 1) can be well explained in terms of the Structure Zone Model [6]. It is well known that the adatom mobility depends on the substrate temperature and surface and bulk diffusion that is characterized by T_s/T_m ratio. Let us consider the case when substrate temperature is about 423 K and deposition rate is about hundred Å/s, the T_s/T_m ratio being about 0.45. So, we fall to Zone T (Transition zone) that is characterized by $T_s/T_m < 0.2$–0.5. During film growth in a mode corresponds to the T Zone area we observe the fine fiber texture development. The saturation nucleation density sets initial in-plane grain sizes. Adatom mobilities are low and columns preserve the random orientation of the nuclei as predicted by the ballistic deposition model [7]. Thus, the crystallites in the film are nearly random or only weakly textured, that is confirmed by X-ray diffraction (Fig. 2c).

The second case is realized when the substrate temperature is 573 K and deposition rate is less than ten Å/s. In this case, T_s/T_m ratio is about 0.61 that corresponds

to Zone II ($T_s/T_m < 0.3$–0.7). Here, the surface diffusion rates are significant, thus, the film thickening proceeds through local epitaxy on individual grains. Moreover, at higher T_s/T_m, the volume diffusion becomes significant. So, the grain coarsening, i.e. recrystallization through grain boundary migration, takes place not only during coalescence, but also throughout the film thickening process. The decrease in the total grain boundary areas as well as minimization of interface and surface energy are the driving forces for orientation selection during the coalescence stage. As a result, the island with lower energy per atom consumes the others, resulting in a new single crystal island, as the system attempts to minimize the overall surface and interface energy. So, large grains with low surface and interface energy grow at the expense of smaller or unfavorably oriented grains. Thus, the coarsening during coalescence is the most probable cause resulting in selection of preferred orientation. So, the film structure is composed of columnar crystals (Fig. 1). In addition, the diffusion processes are not limited by high deposition rate, thus, the single crystalline columnar blocks appear (Fig. 2a). But in case of the substrate temperature 573 K and deposition rate of tens Å/s, a weak limitation of condensed atoms migration on the surface of substrate takes place. This results in deterioration of crystalline perfectness of columnar blocks, the preferred orientations in layer being, however, retained (Fig. 2b).

Appearance of two preferred orientations [110] and [112] in CsI(Tl) films can be explained as follows. As mentioned above, the coarsening during coalescence provides a selection of preferred orientations. The islands terminated with close packed planes are typically selected, that is, (110) for body-centered cubic lattice. Another reason is that (110) and (112) are the particular low index crystallographic planes of body-centered cubic ionic crystals that are neutral.

All diffraction data shown in Fig. 2 were obtained using the θ – 2θ symmetric scanning mode. From these data, we obtain information only about orientations of film planes that are parallel to the substrate. To clarify the orientation of film blocks in lateral direction to the substrate, the X-ray diffraction reflections from inclined crystallographic planes of the substrate and film were examined in asymmetric mode. As a result, relations between (210) and (400)
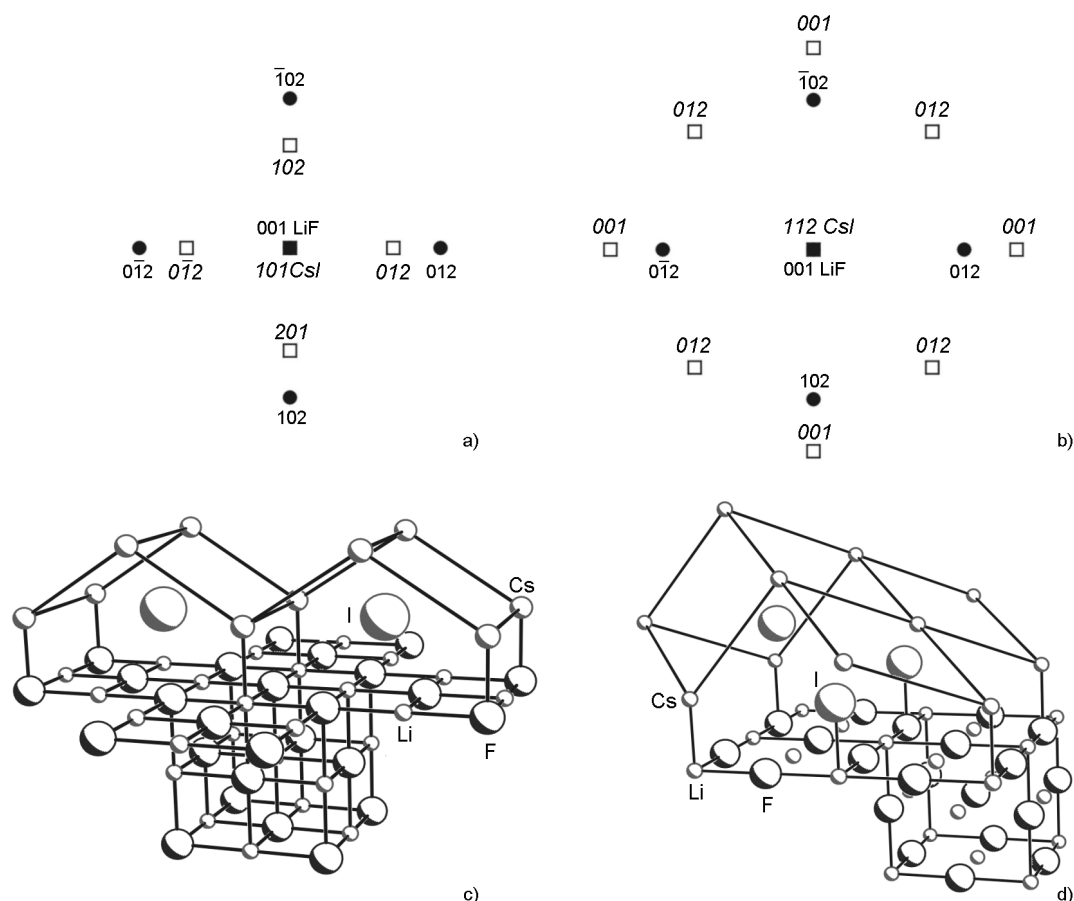
Fig. 3. Stereographic projections of CsI/LiF(100). <110> (a) and <112> (b) layer orientation. Dark dots correspond to LiF and light squares to CsI film. Proposed structure of CsI/LiF(100) interface for (110) (c) and (112) (d) CsI orientation.

film planes inclined to (110) and (112) planes, respectively, and (210) substrate planes inclined to (100) plane were determined. Basing on the data obtained, the corresponding stereographic projections were plotted (Fig. 3a, b). As follows from Fig. 3b, angles between proper reflections from inclined planes of the film and substrate can either coincide with each other or be turned by 45°. Hence, the film blocks of the same orientation can coexist in two equiprobable positions relative to the substrate and the angle between these positions is 45°. Using these data, the model of the film/substrate interface structure was proposed (Fig. 3c, d). From that model, it can be concluded that interaction between CsI and LiF is weak, because only a half of the inversely charged ions of the film and substrate are situated opposite to each other. Therefore, there is balance between repulsion and attraction forces at the interface. This weak interaction between the layer and the substrate and large value of CsI and LiF

lattice misfit provide film growth according to coincident nodes mechanism. As follows from the obtained structural data, at high substrate temperature and rather low condensation rate, the substrate influences on the growing layer structure. This influence is not strong but it is sufficient to order the film columnar blocks accordingly to the substrate in-plane orientation. But at high deposition rate and low substrate temperature, the orientation influence of substrate on the growing layer orientation disappears (Fig. 2c).

CsI(Tl) films deposited onto glass substrate demonstrate a similar dependence of the structure on the deposition conditions. That is, decrease of the substrate temperature from 573 K to 373 K and increase of the condensation rate result in the film crystalline structure change from highly textured to usual polycrystalline CsI structure (Fig. 4). Of course, the absence of orienting substrate prevents the development of the single crystalline areas in the film
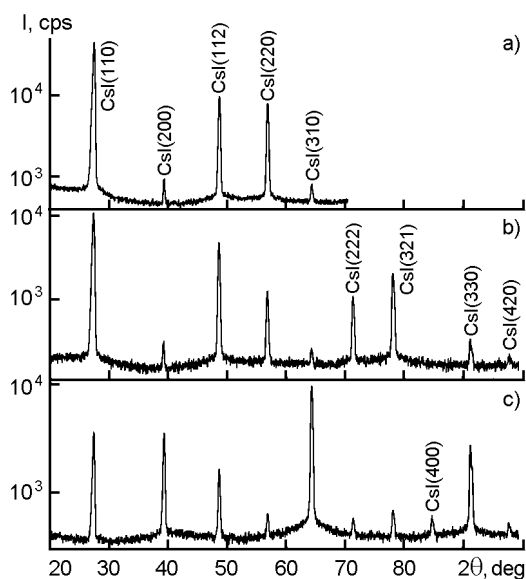
Fig. 4. X-ray diffraction patterns of the CsI(Tl) films deposited on the glass substrate: a) deposition rate 1.3 Å/s, substrate temperature 573 K; b) deposition rate 7 Å/s, substrate temperature 573 K; c) deposition rate 7 Å/s, substrate temperature 373 K.

even at the most favorable deposition conditions.

To achieve the highest possible scintillation efficiency of CsI(Tl) films, the concentration and homogeneous distribution of thallium are essential. In most cases, thallium concentration in the vacuum evaporated CsI(Tl) layers is inhomogeneuos due to the differences of partial vapor pressures of CsI and TlI. In this work, the usual deposition method from powder source was replaced by sublimation of the bulk CsI crystal with optimal Tl concentration. Determination of Tl content in the source had shown that it is constant and equals to 0.1 wt.%, both prior to and after deposition. So we supposed that, at constant Tl content in the source prior to and after deposition, the Tl content in a film corresponds to it of the source. This assumption was confirmed by the voltammetric analysis of Tl content in the film. The Tl concentration in the deposited films was 0.1 wt.%, too. Hence, this technique provides a proper concentration and homogeneous distribution of dopant during deposition.

To compare the scintillation efficiency of CsI(Tl) films deposited from different sources, the scintillation pulse height spectra were obtained. For comparison purposes, all pulse height spectra shown in Fig. 5
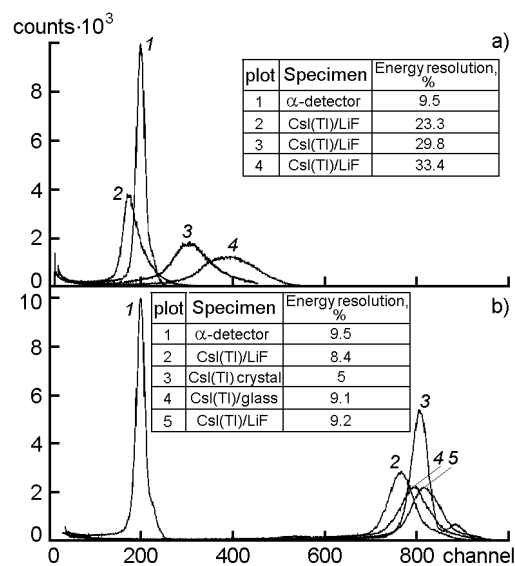

Fig. 5. Pulse height spectra of CsI(Tl) films deposited from different sources: a) CsI(Tl) films deposited from powder source: *2* — thickness 5 μm, deposition rate 1 Å/s; *3* — thickness 10 μm, deposition rate 10 Å/s; *4* — thickness 30 μm, deposition rate 5 Å/s. b) CsI(Tl) films deposited from bulk CsI(Tl) single crystal: *2* — thickness 140 μm, deposition rate 3 Å/s; *3* — single crystal CsI(Tl); *4* — thickness 60 μm, deposition rate 63 Å/s; *5* — thickness 30 μm, deposition rate 5 Å/s. All film spectra are normalized to the α-detector peak.

were normalized to the peak of the standard CsI(Tl) α particle detector. All samples shown in Fig. 5 were deposited under similar conditions to exclude the influence of crystalline structure on the obtained scintillation results. The films were deposited using the same CsI(Tl) crystal with known dopant concentration of 0.1 wt.%. For deposition from powder source, this crystal was powdered and for deposition from the bulk, the bulk part of this crystal was used as source.

As is shown in Fig. 5, CsI(Tl) films deposited from the bulk crystal show a higher energy resolution than the films deposited from powder source. This difference in energy resolution of CsI(Tl) films deposited from various sources can be explained as follows. During deposition from the powder CsI(Tl) source, an inhomogeneous dopant concentration takes place over the volume of growing layer due to the source depletion of Tl during deposition. Therefore, the parts of film with different dopant concentration

respond differently to exciting radiation. This feature results in broadened scintillation pulse height spectra.

As it is seen from Fig. 5, CsI(Tl) films deposited from powder source have lowered light yield as compared to the films deposited from bulk source. This distinction in light yield can be explained by the source depletion of Tl during deposition in the case of evaporation from CsI(Tl) powder. The fact of Tl depletion in powder source during deposition was confirmed by voltammetric analysis. In turn, this Tl depletion in source results in depletion of dopant in the growing layer.

To conclude, it has been demonstrated that the use of CsI(Tl) bulk crystal sublimation during vacuum deposition provides a reproducible dopant content and uniform distribution in the growing films. That, in turn, results in improved scintillation characteristics of CsI(Tl) films, such as light yield and energy resolution, as compared to CsI(Tl) films deposited from the powder source. The dependence between deposition conditions and film crystalline structure is the same both for deposition from bulk CsI(Tl) crystal and for deposition from powder CsI(Tl) source. It has been shown that in both cases, CsI(Tl) columnar layers can be obtained under proper deposition conditions with the single crystalline structure of columnar blocks.

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Плівки CsI(Tl): отримання, дослідження структури та сцинтиляція

О.Лебединський, О.Федоров, А.Ананенко, П.Матейченко

Показано, що застосування сублімації монокристала CsI(Tl) з оптимальною концентрацією активатора замість порошкового джерела при вакуумній конденсації плівок CsI(Tl) дозволяє одержати плівки CsI(Tl) з необхідною концентрацією та однорідним розподілом активатора в об'ємі плівки. Плівки CsI(Tl), отримані з використанням такої технології, демонструють сцинтиляційні параметри, що перевершують параметри плівок CsI(Tl), одержаних за загальноприйнятою технологією. Детально досліджено залежність кристалічної структури плівок від умов осадження.