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Abstract:

A device for the deposition of a radioactive Langmuir-Blodgett (LB) film was developed with the use of: (1) a modified horizontal lifting method, (2) an extremely shallow trough, and (3) a surface pressure-generating system without piston oil. It made a precise radioactive subphase solution repeatedly usable while keeping its radioactivity concentration as high as possible. Any large-size thin films can be prepared by just changing the trough size. Two monomolecular-layers of Y-type films of cadmium [^{109}Cd] icosanoate and ^{109}Cd icosanoate were built up as ^3H and ^{109}Cd β -sources for electron spectroscopy with intensities of 1.5 GBq (40 mCi) and 7.4 MBq (200 μCi), respectively, and a size of 65×200 mm². Excellent uniformity of the distribution of deposited radioactivity was confirmed by autoradiography and photometry.

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1. Introduction

The Langmuir-Blodgett (LB) method [1,2] is a well-known technique for preparing thin organic films. Certain kinds of long-chain fatty acids (of a spreading solution) spread over the surface of an aqueous solution (subphase solution), and form, under fine compression (so-called surface pressure), perfectly lined up molecules in a closely packed monomolecular layer with the hydrophobic side of the molecule up and the hydrophilic side down (see Fig.1). A single layer is transferred (deposited) or "built up" onto a substrate plate by means of the chemical affinity between the molecule and the plate surface; successive transferences then produce a multi-layer. The layers form a structure of one of the so-called X, Y or Z type, depending upon the properties of the molecule, substrate surface, subphase solution, surface pressure, and build-up method. The thickness and uniformity of the film can then be, in principle, controlled in the unit of a monomolecular layer (MML) of $\sim 25 \text{ \AA}$ and having a molecular size of $\sim 20 \text{ \AA}^2$, respectively. The LB-film is therefore commonly employed in the fields of colloid and interface science, micro-electronics and micro-lithography, etc [2].

We have adopted this technique for preparing ^3H and ^{109}Cd β -ray sources for measuring the electron anti-neutrino mass in ^3H β -decay [3]. (Mono-energetic β -rays, from ^{109}Cd decays in our case, are a must for understanding the response function of an entire detection system in precision spectroscopies.) It is because the LB-film is much more superior in respect to uniformities in thickness and lateral directions, compared to sources prepared by other methods, such as vacuum evaporation [4] and ion implantation [5]. In addition, it is reliably reproducible. Radioactive MMLs of LB-films were studied in 1963 by Beischer, who used ^{14}C -labelled [6] or tritiated stearic acids [7] and autoradiography as the most convenient radiation detector. Radioactive nucleides in a MML were in some cases utilized as tracers for studies of the physical and chemical properties of the film [6,8]. In some other cases, an LB-film was employed as a β -ray source with no self-absorption, for instance, in measurements of backscattering phenomena by Beischer [7], K-fluorescence yields of nucleides by Dobriović and Simović [9], and the range of β -rays by Mori et al. [10]. The deposited radioactivity of the films in these studies were quite low, less than a few tens of kBq. Recently, two experimental groups studying the neutrino mass prepared ^3H sources in the same way as ours, but used different acids and build-up methods. The group at Oxford used a tritiated palmitic acid and built up films by a vertical dipping method [11]. Their specific activity and radioactivity concentration in a spreading solution were quite high compared to the above-mentioned cases [6-10], but 370- and 60-times weaker than those in our case (described below), respectively; the resultant deposited radioactivity of 10 MMLs was 0.7 GBq for a source area of 4.25 cm^2 . The other group in Zurich

prepared a single MML source with a tritiated octadecyltrichlorosilane [12]; details, however, have not yet been published. When quite intense radioactive films are built up with high specific activity and radioactivity concentration in solution, relevant new aspects arise and then related technical devices should be contrived, as reported here. In addition to the intrinsic advantages of the LB-film mentioned above, specific features of our sources are as follows:

- For the ^3H source, a tritiated icosanoic acid of the spreading solution is used in the form of Cd salt, a tritiated icosanoate:

where a tritium atom is denoted by T instead of ^3H . To make the acid non-volatile in a vacuum (to prevent the spectrometer from radioactivity contamination and to suppress the background contribution from the volatilized radioactive acid), it was formed as Cd salt by using ordinary (non radioactive) cadmium chloride of the subphase solution.

- To prepare the ^{109}Cd source, an ordinary icosanoic acid with radioactive cadmium chloride was used, but just using the same build-up procedure as that for the ^3H source. (Since the ^{109}Cd source thus had the same chemical structure and the same physical quality as the ^3H source, the measured response function with the former source should be exactly the same as that for the latter source.)

- The sources prepared were of the Y type and having a two MMLs thickness. They were extremely large, $65 \times 200 \text{ mm}^2$, and highly radioactive, 1.5 GBq and 7.4 MBq for the ^3H and ^{109}Cd sources, respectively.

A build-up device was developed by means of a modified horizontal lifting method with an extremely shallow trough and a piston oil-free surface pressure-generating system.

- It was made possible, especially for the ^{109}Cd build-up, to keep the radioactivity concentration in the subphase solution high and to repeatedly use this precious solution for depositions over and over again.

The successful completion of film deposition is usually tested by confirming equalities between [the reduced area of the spread acid] and [the substrate plate area] $\times$ [the number of MMLs built-up] and between the measured and calculated radioactivity intensities of the built-up film. However, these equality measurements are not sufficiently precise to examine the deposition uniformity.

- It was found in our study that the equalities did not always guarantee the successful deposition if a critical amount of certain impurities was contaminated in

the solution as discussed later. X-ray autoradiography and photometry, however, easily and quickly provide direct and detailed information concerning the uniformity in two dimensions as reported in the text.

We would like to describe in detail our deposition device, the build-up procedure, including chemical preparations, the critical conditions necessary for successful deposition, and the radioactivity uniformity of the prepared sources in the following.

2. Preparation Procedure

2.1 Subphase and spreading solutions

The water (hereafter referred to as purified water) used to prepare the solutions and to wash materials at the final stage before deposition was triply purified by: (1) distillation in a glass stiller, (2) deionization through an anion and cation exchange column, and (3) final distillation in a non-boiling quartz-glass stiller with an infra-red lamp. Organic solvents, benzene and hexane, were also distilled using a non-boiling quartz-glass stiller prior to use. The reagents of cadmium chloride (purity >99.9%, Wako Chemicals, Japan) and icosanoic acid (purity of 99.5%, Fulka AG, Switzerland) were of the commercially-available purest grade and thus used without further purification.

³H source

The tritiated [5,6,8,9,11,12,14,15-³H] icosanoic acid for the spreading solution had a concentration of 1.11 GBq/ml benzene, corresponding to a specific activity of 7.4 TBq/mmol, which was almost the theoretically achievable maximum. This acid was supplied by the Radiochemical Center, Amersham (RCC), England. It was prepared by the catalytic reduction of [5,8,11,14] icosatetraenoic acid using tritium gas, and purified by reverse-phase high-performance liquid chromatography. The radiochemical purity was 98%, measured by three methods: high-performance liquid chromatography on an Ultrasphere ODS (octadecyl silane) column eluted in methanol:acetic acid (1000:1), thin-layer chromatography on silica gel in dichloromethane:1,2-dimethoxyethane:acetic acid (94:6:0.5), and thin-layer chromatography on Whatman KCl18 reverse-phase plates in methanol:water (95:5). To avoid radiolytic or chemical decomposition of the material itself, it was transported by air as a frozen benzene solution at a temperature lower than -20°C and at a concentration of 10⁻⁵ mol benzene. The deposition was performed quickly just after it had been delivered and chemically adjusted as follows using the device shown in Fig.2.

An amount of 10 ml with 11.1 GBq of this solution was transferred to flask-I

and frozen again with dry-ice methanol. By connecting to an empty flask-II, it was evacuated to 10 Pa while being kept in the frozen state by dry-ice methanol. After evacuation flask-II was soaked in liquid nitrogen while flask-I was kept at room temperature. The frozen benzene in flask-I was then sublimated and trapped in flask-II. Consequently, the tritiated icosanoic acid was dried up in flask-I and dissolved again by adding 300 µl benzene to be 3×10⁻³ mol; thus, the spreading solution was ready to take place in three times depositions.

The subphase solution was prepared by dissolving the reagent CdCl₂ in purified water to 10⁻⁴ mol cadmium chloride.

¹⁰⁹Cd source

The subphase solution was prepared from 370 MBq of a carrier-free ¹⁰⁹Cd in a dilute hydrochloric acid solution of 1 ml, purchased from RCC, Amersham. Trace element analysis data indicated the contents of the chemical impurities to be Al³⁺, Fe³⁺, and Ca²⁺ ions at less than a few µg/ml; other ions, such as Co²⁺, Cr³⁺, Cu²⁺, Mn²⁺, Ni²⁺, and Zn²⁺, were much less than µg/ml in order of magnitude, though exact amounts of these individual contents depended on the purchased samples. Using the device illustrated in Fig.3, it was first evaporated to dryness. The residue containing ¹⁰⁹Cd was then dissolved in purified water, and adjusted to 90 ml of 10⁻⁴ mol cadmium chloride solution by adding a reagent, CdCl₂. This was poured at just the right amount into a trough which will be described later.

When the ¹⁰⁹Cd subphase solution was once used for deposition as described below, it was purified so as to remove any possible contamination of organic materials, especially residual icosanoate due to repeated use. The solution recovered after depositions was put into an extraction tube (Fig.4) and acidified to pH~1 in order to dissociate cadmium icosanoate into Cd²⁺ and icosanoic acid by adding several drops of concentrated hydrochloric acid. Organic solvent, 200 ml of ethyl ether, was poured into a flask and heated to 50°C in a water bath. The evaporated ether was transformed into liquid again through a cooling process in a condenser and dropped into the solution through a small glass-tube in the center of the extraction tube. Organic impurities contained in the solution were then removed into the ether. This purification with ethyl ether was continued for more than 20 hours; the resultant solution was treated in the same way as described in the above paragraph.

The spreading solution of the icosanoic acid was prepared to be 3×10⁻³ mol by dissolving the reagent icosanoic acid in benzene.

The pH of the subphase solutions for both sources was adjusted to be 7.0±0.1 by adding a small amount of sodium hydroxide (special grade reagent, Wako Chemicals).

The conditions of the spreading and subphase solutions are summarized in Table 1.

2.2 Deposition device

A schematic drawing of the deposition device is shown in Fig. 5. The left-hand side is a build-up system with a modified horizontal lifting method; the right-hand side is the surface pressure-generating system.

Surface pressure generating system

A silk thread of 0.1 mm ϕ separated the molecules from a movable mica float with a size of 20 $\times$ 190 mm 2 and 0.1 mm thickness. In order to closely compact the molecules into a well-ordered MML solid phase, a surface pressure was generated on the molecules through a mica float and controlled as follows. Dust-free air was conducted from a blower through a HEPA (High Efficiency Particulate Air) filter to a square-shape aluminum pipe 25 cm long with small holes of 0.6 mm ϕ at every 10 mm interval. The air pressure was adjusted in such a way that it would make a 30 g-lucite stand float placed on the pipe. With an adjustment of the pipe's slope the stand slowly came down along the pipe without friction; this force was transferred to the mica float through a piano wire 40 cm long and 0.3 mm ϕ . It generated a constant surface pressure whose strength was controlled continuously and precisely by changing the pipe's slope with screws of the bottom plate (Fig. 5).

The thus-generated surface pressure was calibrated using several kinds of the so-called piston oils known to yield certain constant pressures, such as oleic acid (29.5 mN/m), ethyl myristate (20.7 mN/m), and castor oil (16.5 mN/m): The pressure was generated on the mica float to create a balance against the oil spread on the opposite side separated by the silk thread. A 1 mm rise of one end of the pipe corresponded to a pressure rise of 7 mN/m. The surface pressure for deposition was set to be 30 mN/m as discussed in next section.

The mica float and the silk thread were made to be hydrophobic by coating their surface with paraffin.

Substrate plate

The substrate plate to be used as a resistive electrode plate in our electron spectroscopy had a size of 65 $\times$ 200 $\times$ 1 mm 3 . It was made of an alumina plate (Al_2O_3) with a surface fine smoothness of a few μ m, coated by a mixture of ruthenium oxide (RuO_2) and glass with a thickness of 13 μ m. The plate was washed in organic solvents, acetone and benzene; afterward the surface was treated so as to be hydrophobic by coating it with iron(III) octadecanoate (the purest grade, Tokyo Kasei Industry Co., Japan).

Trough

A trough with an area of 200 $\times$ 210 mm 2 was made of Teflon, since the organic contamination would obstruct successful deposition. The depth of the trough for the ^{106}Cd source was made as shallow as possible, 0.7 mm. This was done so as to concentrate enough ^{106}Cd in a small amount of the subphase solution for building up a highly radioactive film, and also to prevent the mica float from scratching the bottom of the trough. Since the aqueous solution could not fully spread out in a hydrophobic inside of such a shallow Teflon trough, the inner surface was treated so as to be hydrophilic by means of a glow discharge in an oxygen atmosphere of 0.1–0.01 Pa for 1 hour [13]. However, rims of 10 mm wide were kept hydrophobic in order to utilize the surface tension for filling up with the subphase solution. After the glow discharge, the trough was soaked in trichloroethylene for several days in order to remove the oil-mist and other dust, and was then washed with purified water; 90 ml of the subphase solution was necessary to fill up the trough.

For the 3H source preparation, the trough depth was made to be 5 mm, which needed no glow-discharge treatment since a stable subphase solution could be prepared in any amount.

Many Teflon rods with a cross-section of 8 $\times$ 8 mm 2 and 25 cm-long were prepared and used to sweep the dust out from the subphase solution surface, as usual [2]. Those rods were chemically cleansed in the same way as the trough.

2.3 Build-up procedure

The trough was set horizontally; the rotary axis (seen in Fig. 5) was set horizontally and parallel to and near the trough inner edge on the opposite side of the surface pressure-generating system. The substrate plate was attached to a small platform on a rotary axis which could be rotated around the plate's long side edge by the motor system. The influence of mechanical vibration was not visible on the solution surface of the trough.

Since the deposition device was relatively small, it was placed in a lucite box and then in a draft under reduced pressure. This was a precaution to avoid any radioactive contamination of the experimental room and to keep the system free from dust. All of the elements, especially the mica float, silk thread, substrate plate and trough, were kept as clean as possible so as to avoid any chemical impurity. The cleanliness of the subphase solution was scrutinized just before instant of the acid spread, though it was difficult to quantitatively evaluate, by producing a smooth arrival of the mica float at the end of the trough with the exertion of only a few mN/m surface pressure.

The trough was filled with cadmium chloride solution after pH adjustment. The subphase surface was swept with the Teflon rods more than twenty times. The silk thread was made to float on the solution surface, and both ends settled on the trough rims with small glass rods treated so as to be hydrophobic. The mica float was then placed on the subphase surface at the side of the pressure-generating system, and the benzene solution of icosanoic acid was gradually dropped from a microsyringe and dispersed on the other surface. A surface pressure of 30 mN/m was then applied to the mica float in balance with that of the acid molecules. We waited for 10 minutes at this stage for the benzene to evaporate completely and for equilibrium between MML and the subphase solution to be established.

The substrate plate was lowered manually by using a mechanical handle to let the lower end of the plate gently touch the solution surface (Fig.1(b) and Fig.6(a)). It was then smoothly rotated down around the plate's lower end by a motor operation until the entire plate surface came into contact with the solution (Fig.1(c) and Fig.6(b)). After this, the same but reverse process was made (Fig.1(d,e) and Fig.6(c,d)). The speed of the moving mica float was set at 10 mm/min, which was judged to be the optimal condition as mentioned in next section. One deposition (see photographs in Fig.6) took 30–40 minutes for the whole series of procedures described above.

The residual acid on the surface was removed after the deposition in order to carry out successive build-up, since the acid molecules once compacted did not form the MML together with the newly spread acid on the surface. Several mN/m of the surface pressure was applied and the residual was manually taken away by depositing on a metal plate, which was treated in the same way as the substrate plate. When the mica float reached the edge of the trough and the silk thread dominated no appreciable space, the residual was considered to have been thoroughly removed.

After the deposition, the prepared sources were subjected to a pressure of 60 Pa for 5 minutes in order to remove any radioactivity element not strongly bound in the form of built-up cadmium icosanoate, if it existed. Next, they were immediately brought into an experimental source chamber to be evacuated to 10^{-3} Pa and cooled down to -35°C .

3. Uniformity of Deposited Radioactivity

The equalities between the areas of the built-up film and the swept surface by the mica float and between the measured and expected deposited radioactivities are often pointed out as indications of a successful deposition. However, a measurement of the radioactivity distribution by means of autoradiography provides more direct and detailed information concerning the uniformity of the built-up film as explained in the

following.

An X-ray film of RX-type (Fuji Film Co. Tokyo), covered by a Mylar sheet of 3 μm thickness to prevent any radioactive contamination, was put on the prepared ^{109}Cd source and exposed for 10 minutes. The Mylar sheet did not damage the source. The autoradiography was repeated for the same ^{109}Cd source but the sheet was changed every time; no appreciable difference was observed among them. On the other hand, for the ^3H source a film of LKB2208 Biofilm (Amuko Co. Ltd, Tokyo) was exposed for 2–5 minutes without a Mylar sheet, since emitted β -rays of very low energy failed to penetrate it.

Fig.7(a) shows a developed film for the ^{109}Cd source; a uniform distribution of darkness is observed. The photometry result shown in Fig.7(b) was obtained by the use of a microphotometer (MD-II type) with a 200 μm wide slit and a 20 mm/min. scanning speed. The measured intensity of darkness is proportional to the radioactive strength; the tiny bumpy structure of the intensity was due to original stains of the X-ray film. Scans of many different regions along two axes indicated no irregular intensity distribution any more than a stain size, $\leq \pm 1\%$ of the full intensity. We are therefore convinced that the deposited radioactivity was uniformly distributed and complete MMLs were built up.

The X-ray autoradiograph easily provided two-dimensional detailed information concerning the uniformity; the deposition condition was then quickly judged so that appropriate action, if needed, could be taken for the next deposition. Although this method was of macroscopic ($\sim 100\ \mu\text{m}$) and of not microscopic ($< 1\ \mu\text{m}$) accuracy, it was precise enough from most electron spectroscopic considerations.

4. Discussion

4.1 Deposition conditions

The optimal conditions and related aspects for the deposition are described below.

pH

Metal-ion bindings in MMLs of icosanoic acids saturate and form a complete metal soap at $\text{pH} > 6.5$, as observed in Refs.[14–16]. However, the production and precipitation of $\text{Cd}(\text{OH})_2$ was anticipated to occur at $\text{pH} > 8$. Therefore, the pH of the subphase solution was adjusted to 7.0 ± 0.1 to form a complete metal soap with Cd^{2+} , but not undesirable ions, such as Al^{3+} , Fe^{3+} and Ca^{2+} , contaminated in the purchased ^{109}Cd solution. While the pH tended to be reduced by absorbing carbon dioxide in the air, it was 6.9–7.0 after deposition of 30–40 minute duration under our circumstances.

Temperature

It is generally known that the chemical binding force for building up an LB-film becomes weaker due to the thermal motion of acid molecules at temperatures higher than $\sim 20^{\circ}\text{C}$ and the film, on the other hand, tends to harden at temperatures lower than $\sim 15^{\circ}\text{C}$. These exact temperatures depend upon the individual acids and their build-up conditions, although no systematic investigation has yet been carried out. Fig.8(a) shows autoradiographs of the ^{109}Cd build-up source at different temperatures. The uniformity of deposited radioactivity was destroyed at 25°C . The temperature of the experimental room and all of the deposition elements, including the solutions, were therefore kept within a range of $17\text{--}20^{\circ}\text{C}$.

Surface pressure and build-up speed

According to Kobayashi and Takaoka [14], the pressure was set to be 30 mN/m . Although the tolerable pressure range is wide, especially due to the crosslinking effect of metal soap as described in Ref.[2], the constant pressure as realized by our system is important for uniformly compactifying the molecules to a solid phase.

The speed was limited to less than 10 mm/min in terms of the mica float movement, since the film, especially the second MML, was sometimes peeled off at a speed of 20 mm/min [17]. The area peeled was clearly observed by autoradiography and exhibited just a half darkness of two MMLs in photometry.

Cadmium and acid concentrations of the solutions

The intensity of deposited radioactivity was measured as a function of the cadmium chloride concentration of the subphase solution, and saturation was observed at more than 10^{-4} mol . This is consistent with the data for a complete formation of the cadmium icosanoate at the same concentration as that measured in Ref.[16].

The acid concentration of the spreading solution, typically $\sim 10^{-3}\text{ mol}$, was not a critical parameter, as long as the solvent dissolved an adequate acid quantity without reacting chemically with the subphase solution and completely evaporated within a reasonable period of time. A concentration of $3\times 10^{-3}\text{ mol}$ was chosen so as to aid the spreading process to come to completion within a 10 minute duration.

Chemical impurities of the subphase solution

The contamination of triply and doubly charged ions, especially Al^{3+} , Fe^{3+} and Ca^{2+} , of the 1 ml hydrochloric acid solution of ^{109}Cd purchased from RCC, Amersham, ranged from a few tenths to a few $\mu\text{g/ml}$, which strongly depended upon the individual samples. Wolstenholme and Schulman [18] found with the use of a myristic acid that

the Al^{3+} and Fe^{3+} ions yield hydroxide precipitation at $\text{pH}>6$ and 5 , respectively; furthermore, the latter does not form any solid film at $\text{pH}>5.5$. The Ca^{2+} ions, on the other hand, form a metal-soap at $\text{pH}>5.5$ and would not precipitate at $\text{pH}=7$. We supposed a similar trend regarding the charged ions also in icosanoic acid; the Al^{3+} and Ca^{2+} ions make the film rigid and the deposition difficult, as follows. When some of the samples were diluted with only one tenth of the usual reagent CdCl_2 amount, the mica float moved only less than half of the normal span in the deposition; the resultant deposited activity was forty-times weaker than the normal value, as an extreme case. When the samples were normally diluted to a concentration of 10^{-4} mol , the float moved as usual and uniform deposition was achieved most of the time. The ion concentrations of the normal solution were less than $(1\text{--}2)\times 10^{-6}\text{ mol}$.

Although the mica float swept the solution surface twice the size of the substrate plate and the measured deposition radioactivity agreed with the expected value, non-uniform deposition, especially for the ^{109}Cd source, was only sometimes detected by X-ray autoradiography, as shown in Fig.8(b). This was probably due to a critical amount of the contained impurity ions mentioned above, as the uniform deposition was recovered when the solution was diluted with additional reagent CdCl_2 . This critical rate of the contamination, predominantly of Al^{3+} and Ca^{2+} ions, was then estimated to be $\sim (\text{a few})\times 10^{-6}\text{ mol}$ as an order of magnitude.

Self-decomposition of tritiated icosanoic acid

Due to the high specific radioactivity, the acid easily self-decomposed [19]. Whenever the self-decomposition took place due to a time lapse between delivery and deposition, the mica float would not stop at the expected position under the normal surface pressure.

Residual acid

The effect of residual acid was examined with and without its thorough removal after deposition. An autoradiograph for the latter case is shown in Fig.8(c).

4.2 Specific features of the device

A highly radioactive carrier-free solution is commercially available, though generally quite expensive. Its cost can be reduced if prepared by the customers themselves, although the purification process is very complex and time consuming. Most such precious solvent is used up in a single deposition. For instance, in vacuum evaporation the deposition efficiency is generally less than 10% with an inferior uniformity compared to the LB-film. Our device, on the contrary, makes it possible to effectively reuse the

substance many times without any appreciable loss of radioactivity.

A commercially available built-up device (usually by a vertical dipping method of substrate plate under an electronically controlled surface pressure) is fairly expensive and not quite small compared to ours. If once contaminated by radioactivity, it cannot be used for the deposition of other radioactive or non-active elements unless the contamination is sufficiently removed. Our extremely shallow trough was small sized and disposable. Therefore, the trough and all elements, except for the surface pressure-generating system and the motor-driven plate lifting system, were replaced after each set of depositions.

Our modified horizontal lifting method simply avoided undesirable radioactive contamination of the opposite side of the source plate.

Any large size of excellently thin and uniform radioactive LB-film can be prepared by just changing the size of the trough; however, it is impractical to obtain such a quality of a large sized source by other source preparation methods.

4.3 Non-volatility in vacuum

While the LB-film is in general volatile in a vacuum, it becomes resistive against volatility when formed as a metal soap, as studied by Roberts and Gaines [20], Schonhor [21], Kobayashi and Takaoka [14], and Spink [22]. The evaporation rate of ^3H molecules in a vacuum was measured for the built-up cadmium [^3H]icosanoate MMLs with various specific activities and temperatures. The details of the measurement was reported in Ref.[23]. With [^3H]icosanoate of 185 GBq/mmol specific activity, the rate for films with 2, 4, 6, and 8 MMLs was $\sim 1\%$ per week under a pressure of 1×10^{-4} Pa and a room temperature of 15°C . In the case of the highest specific activity of 7.4 TBq/mmol, the rate was $\sim 1\%$ per one day. When it was cooled down to -100°C , the rate was extremely reduced to less than 10^{-4} over a 10 day period and no appreciable time dependence was found. The sources was cooled down at -35°C in a vacuum of 10^{-4} Pa for the neutrino mass measurement, and no serious radioactivity contamination of the spectrometer and no increase in the background contribution with time were detected during several months of measurements.

5. Summary

We developed an LB-film deposition device by means of a modified horizontal lifting method. Our use of an extremely shallow trough and a piston oil-free surface pressure-generating system allowed repeated use of the precious radioactivity subphase solution possible, and kept its radioactivity concentration high with only a small amount of

solution.

The X-ray autoradiography with its quantitative evaluation by photometry was demonstrated to be a simple, easy and direct method for examining the quality of deposited films.

Two monomolecular layers of Y-type films were built-up with cadmium [^3H]icosanoate and ^{109}Cd icosanoate as ^3H and ^{109}Cd β -sources of the same quality, respectively, for neutrino mass measurements. The sources had a large size of $65 \times 200 \text{ mm}^2$ and high radioactivities of 1.5 GBq for ^3H and 7.4 MBq for ^{109}Cd . The excellent uniformity of these sources was confirmed by X-ray autoradiography. The surpassing performance of these thin LB-films as β -ray sources was demonstrated not only by neutrino mass measurements [3], but also by spectroscopies of the KLL, KLM and KLN Auger electrons [24] and an energy-loss measurement of β -rays in a thin material [25].

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Tables Caption

Table 1: Deposition conditions of spreading and subphase solutions for ^{109}Cd and ^3H LB-film sources.

	^{109}Cd Source	^3H Source
Source material	^{109}Cd icosanoate	cadmium [^3H] icosanoate
Spreading solution	$100\ \mu\text{l}$ of 3×10^{-3} mol icosanoic acid in benzene	$100\ \mu\text{l}$ of 3×10^{-3} mol [^3H]icosanoic acid in benzene containing $3.7\ \text{GBq}$ of ^3H
Subphase solution	$90\ \text{ml}$ of 10^{-4} mol CdCl_2 in pure water containing $370\ \text{MBq}$ of ^{109}Cd	$650\ \text{ml}$ of 10^{-4} mol CdCl_2 in pure water
Trough size	$200\times 210\times 0.7\ \text{mm}^3$	$200\times 210\times 5\ \text{mm}^3$
Subphase solution pH	7.0 ± 0.1	7.0 ± 0.1
Subphase solution temperature	$17\text{--}20^\circ\text{C}$	$17\text{--}20^\circ\text{C}$
Surface pressure	$30\ \text{mN/m}$	$30\ \text{mN/m}$

Figure Captions

Fig.1: Illustration of the LB-film and its deposition procedure. (a): A long-chain fatty acid on an aqueous solution forms a closely packed monomolecular layer (MML) under a fine compression by a surface pressure. (b-e): A hydrophobic and hydrophilic part of the molecule are shown by the line and open circle, respectively, and the surface pressure is indicated by the arrow from the right-hand side. The MMLs are deposited by means of a horizontal lifting method modified for building-up two MMLs of Y type. The first MML is transferred onto a plate by means of hydrophobic affinities between the molecules and plate surface, (b) and (c). The second layer is next built-up by the hydrophilic affinities between the molecules of two MMLs, (d) and (e). (f): Two MMLs of Y type film thus prepared with the use of cadmium icosanoate is illustrated, where the Cd^{2+} ions are indicated by closed circles.

Fig.2: Device for evaporating benzene solution of tritiated icosanoic acid in vacuum. Tritiated acid remained in the flask-I and the benzene was trapped in flask-II. See the text for detail.

Fig.3: Device for evaporating a hydrochloric acid solution containing carrier-free ^{109}Cd . It evaporated the acid solution leaving CdCl_2 as a residue.

Fig.4: Device for purifying a ^{109}Cd subphase solution. The evaporated ether removed organic impurities of the subphase solution, which was recovered after a series of depositions. The resultant solution was evaporated to dryness with the device shown in Fig.3.

Fig.5: Device for depositing an LB film. The left-hand side illustrates a modified horizontal lifting system comprising a shallow Teflon trough, a substrate plate holding arm, and a plate rotation system with motor-drive and manual movements. The right-hand side is the surface pressure-generating system. An air-floated lucite stand forces a movable mica float to compactify spreading acid molecules to form a monomolecular layer. The device is placed in a lucite box and then in a draft under a reduced pressure for precaution of an experimental room against radioactive contamination and a solution surface against dust. See the text for details.

Fig.6: Photographs of the deposition procedure: (a) The edge of the substrate plate, at the left-hand side, is just touching a surface of the subphase solution. Shown at the right-hand side is a movable mica float forced by a piano-wire to compress

the acid molecules. (b) The entire plate surface completely come into contact with the solution surface. (c) The plate is rotated back about half a way. The mica float sweeps the area of the solution surface corresponding to the transferred area of acid MML onto the plate. (d) Same as (a), but after the deposition of two MMLs. The mica float has moved a distance of just two times the plate width.

Fig.7: A sample of (a) autoradiography and (b) photometry for a uniform ^{108}Cd source deposited at a temperature of 20°C . The size of the LB-film was $65\times 200\text{ mm}^2$. Scans of photometry were performed along both directions, as indicated in the sub-figure in (b). The tiny bumpy structure of the lines in (b) was due to original stains in the X-ray film.

Fig.8: Autoradiographs for non-uniform ^{108}Cd sources. (a) is for a source built-up at a temperature of 25°C . Sources built-up at different temperatures of 20°C and 17°C yielded uniform radioactivity distribution. As an example, see Fig.7(a), which was deposited at 20°C . (b) This non-uniformity of deposited radioactivity is suspected to be due to a critical amount of impurity contamination, predominantly of Al^{3+} and Ca^{2+} ions. (c) is for a source built-up without any thorough removal of the residual spread acid.

Fig. 1

Fig. 2

Fig.3

Fig.4

Fig.5

Fig.6

(c)

(d)

Fig. 6

(a)

Fig. 7

Fig. 7

Fig. 8