

INTEGRABLE LITHIUM SOLID-STATE MICROBATTERIES

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Summary

Thin, micro-solid-state lithium batteries using lithium borate glass as electrolyte and InSe, In₂Se₃ layered cathodes have been obtained recently by flash evaporation or molecular beam deposition techniques.

Thin cells grown by flash evaporation, having an area of 1 cm² and a cathode mass of 2 mg, present an average OCV of 1.6 V, giving a practical capacity of $Q = 38 \mu\text{A h}$, corresponding to a volume capacity of 57 A h l⁻¹.

Molecular beam deposited cells having an In₂Se₃ cathode 3.5 μm thick show an OCV of 1.2 V.

1. Introduction

Over the past ten years a spectacular development has been seen in the microelectronic industry but, to date, the application to integrable power sources has still not been realised. The feasibility of thin-film, solid state batteries is of great interest in view of developments in the field of micro-ionic technology. A few microionic applications may already be mentioned: two good examples are the elaboration of integrated gas sensors [1] and the microcoulometric system [2].

Cells with thin-film electrolyte [3] and electrode [4] materials have been investigated recently. Consistent effort has been applied to the development of a complete thin-film, solid-state battery [5, 6], and the most promising seems to have been that of Kanehori *et al.* [5]. This battery, however, faces two major difficulties: (i) the mechanical stability of the intercalation cathode TiS₂ deteriorates after a large number of cycles; (ii) the inflexibility of the electrolyte material reduces its capacity to accommodate the volume expansion of the cathode after intercalation. The major problem is still the requirement for perfect physical contact between the solid electrolyte and the electrode.

From a critical examination of previous attempts to build thin-film, solid-state batteries, we have concluded that the key factors are the

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electrode–electrolyte interface and the mechanical properties of both the electrolyte and the electrode. The wetting conditions of a liquid–solid interface are not necessarily suitable for a solid–solid interface. Therefore, we believe that in solid-state devices we must aim for a clean, reactive electrolyte surface on which to graft the cathode material by molecular beam deposition (MBD).

This paper describes the first attempt to construct a solid-state battery using molecular beam deposition throughout the process. In this presentation we discuss results mainly obtained by MBD on the intercalation cathode material In_2Se_3 or InSe , and on the electrolyte, fast ion conducting glass $\text{B}_2\text{O}_3-x\text{Li}_2\text{O}$. The electrochemical properties of InSe films fabricated by flash evaporation are also presented.

2. Molecular beam deposition

Molecular beam deposition (MBD) is a versatile evaporation technique which can be used to prepare compound semiconductor, elemental semiconductor, metal and insulating layers. It is distinguishable from other methods because of the more precise control of the beam fluxes and deposition conditions.

The main advantage of the MBD process lies in the possibility of building the electrolyte–electrode interface in ultra high vacuum (UHV) and this special environment leads to the possibility of having a perfectly clean interface. If the electrolyte surface is properly cleaned, the changes of having a reactive, pure interface are quite good.

Figure 1 shows a schematic diagram of the MBD system where an entire solid-state microbattery may be constructed. The procedure starts with the growth of a thin film of a layered compound of the In–Se family in a Riber molecular beam epitaxy chamber under UHV of 5×10^{-11} Torr. In practice, during growth the total pressure in the reaction chamber may rise to the region of 7×10^{-11} Torr due to selenium. The growth of the second layer, *i.e.*, the electrolyte thin film, and the final step, *i.e.*, the elaboration of the lithium anode film, are performed in the MECA 2000 MBD chamber.

In addition, under the same clean atmosphere conditions, surface studies such as reflection high energy electron diffraction (RHEED) analysis, and electron spectroscopy such as Auger electron spectroscopy (AES) or photoelectron spectroscopy (XPS) are desirable when investigating the structural and electronic surface states of compound semiconductors. These three techniques and a quadripolar mass analyser are installed in the system shown in Fig. 1. Finally, the system is connected to a glove-box which allows the lithium effusion cell to be loaded and to receive the elaborated micro-battery for testing purposes.

Growth conditions of the cathodic compound

The growth conditions for molecular beam deposition of the In–Se thin film have been investigated, and the film stoichiometry controlled by the

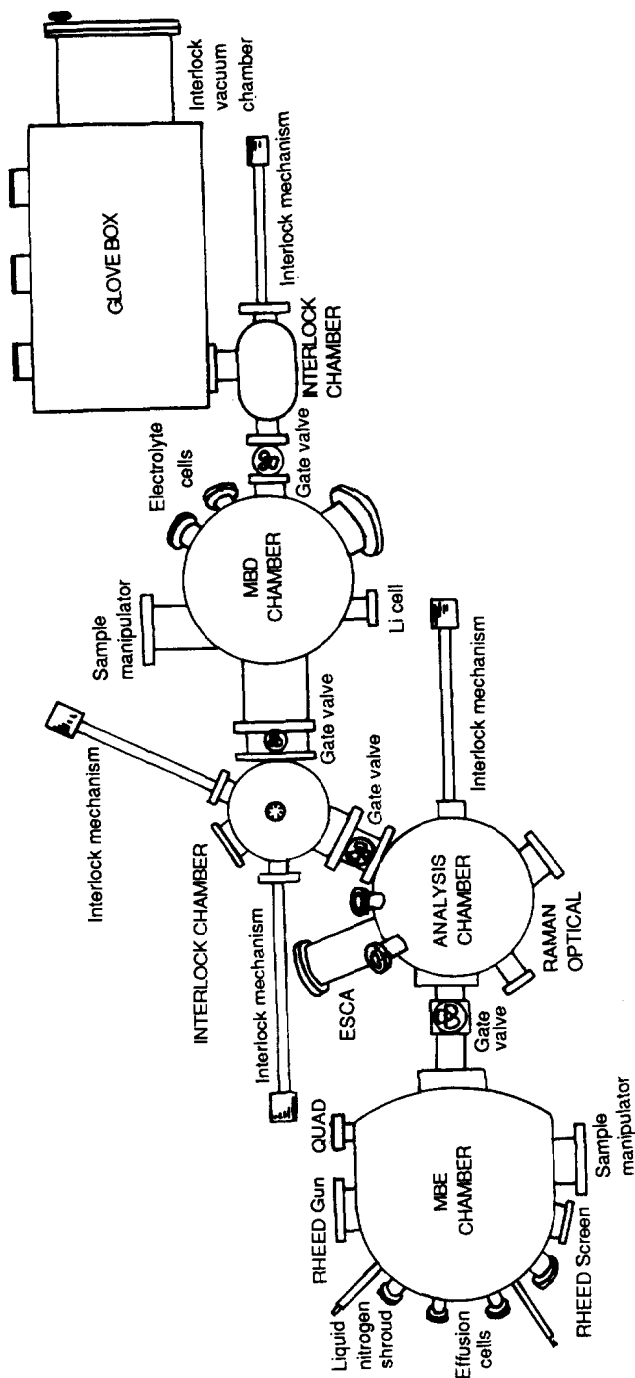


Fig. 1. Molecular beam deposition schematic diagram.

flux ratio which is obtained from pressure measurements prior to growth. The film is deposited on a silicon (100) wafer which is fixed onto molybdenum substrate heater blocks. Silicon substrates having low electrical resistivity were cleaned by both an external oxide-removal procedure and an *in situ* thermal treatment. The depositions took place in the range 300 nm h^{-1} - 2000 nm h^{-1} . The final thickness was in the range $0.5 \text{ }\mu\text{m}$ - $4.5 \text{ }\mu\text{m}$. Depending on the flux ratio $R = P_{\text{Se}}/P_{\text{In}}$, two different phases can be obtained: for $R < 3.6$ the InSe polycrystalline phase alone is observed, whereas for $R > 5$ the In_2Se_3 polycrystalline phase is obtained. In the intermediate regime, an amorphous InSe thin film is fabricated which, after an appropriate thermal annealing at $300 \text{ }^\circ\text{C}$ for 3 h, becomes somewhat polycrystalline.

The characterization of the films was made by XPS, and their structure was determined by Raman spectroscopy. Figure 2 shows the Raman scattering (RS) spectra of cathodic films $1 \text{ }\mu\text{m}$ thick grown at $T_s = 300 \text{ }^\circ\text{C}$ using various beam flux ratios. For values higher than $R = 5$, the $\gamma\text{-In}_2\text{Se}_3$ phase is identified by means of the lines at 153 and 232 cm^{-1} [7]. Decreasing R results in the appearance of the InSe polycrystalline phase only, and for $R < 4$, the peaks between 170 and 235 cm^{-1} are very well defined. The results obtained on an as-deposited film and an annealed InSe thin film lead to the following conclusion: annealing a film grown with $R = 2.7$ does not increase its crystallinity, while a thermal annealing process clearly improves the crystallinity of InSe films grown under Se-rich conditions.

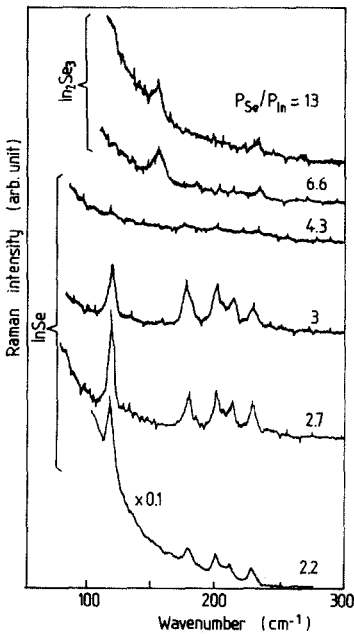


Fig. 2. Raman scattering spectra of In-Se thin films deposited by MBD recorded using a Ar^+ laser at 514.5 nm . The ratio of the elemental fluxes is given for each film.

Growth conditions of the electrolyte

Solid electrolyte $B_2O_3-xLi_2O-yLi_2SO_4$ ($x < 0.6$, $y < 0.3$) amorphous films were deposited at a rate of $0.45 \mu\text{m h}^{-1}$ on the InSe cathode film under the same conditions as those used for the InSe film. For a thin film of borate glass to be useful as a solid electrolyte two conditions are necessary: (i) the film should be an excellent electronic insulator, and sufficiently thick to avoid shorting, (ii) the thin film should be a very good ionic conductor. Thin films of $Li_2O-B_2O_3$, Li_2O-SiO_2 and $Li_2O-P_2O_5$ binary systems have been prepared in the amorphous state, by conventional vacuum deposition procedures, in the past [8].

In order to determine reproducible conditions for glass electrolyte evaporation we have investigated the main growth parameters: the source temperature T_c , the substrate temperature T_s and the evaporation rate. The relationship between the composition of thin films of the $Li_2O-B_2O_3$ system and the processing conditions was studied by analysis of the far-infrared spectra of films deposited on silicon wafers (Fig. 3).

The peaks at 1000 and 1400 cm^{-1} , which are attributed to the B—O bond stretching of tetragonal BO_4 and trigonal BO_3 , respectively [9], are lithium oxide content dependent and the measurement of their ratio is directly connected to the increase in conductivity of the superionic glass conductor. From these studies we conclude that:

(i) the lithium content in the deposited film is lowest when the substrate temperature is higher;

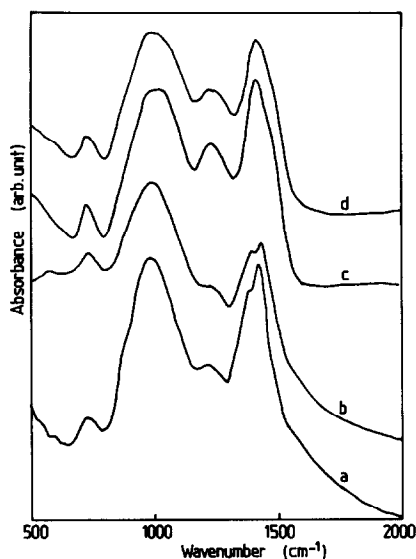


Fig. 3. Infrared absorption spectra of different borate glass thin films obtained under different conditions: at $T_s = \text{RT}$ (a, b, c); $T_s = 200^\circ\text{C}$ (d); $T_c = 720^\circ\text{C}$ (a); 870°C (b); 950°C (c, d).

- (ii) the lithium content in the film is independent of the evaporation source temperature for $T_c < 1000\text{ }^\circ\text{C}$;
- (iii) it is also independent of the substrate temperature.

3. Integrable lithium solid state microbatteries

Thin, micro-solid-state lithium batteries (cell A) using lithium borate glass, $\text{B}_2\text{O}_3\text{-}0.8\text{Li}_2\text{O}$, as electrolyte and an In_2Se_3 cathode have been obtained by the MBD technique. The cathode, $3.5\text{ }\mu\text{m}$ thick, which was obtained at a rate of $0.6\text{ }\mu\text{m h}^{-1}$ from the In and Se Knudsen cells at 820 and $175\text{ }^\circ\text{C}$, respectively, is in the In_2Se_3 polycrystalline phase. The $1\text{ }\mu\text{m}$ thick electrolyte film was made from lithium metaborate, BLiO_2 , evaporated at $770\text{ }^\circ\text{C}$, while the metallic lithium anode film was fabricated at the high rate of $5\text{ }\mu\text{m h}^{-1}$ from a boat heated at $500\text{ }^\circ\text{C}$. The open circuit voltage of the cell shows a plateau at 1.2 V which is similar to that observed using a powdered cell, but the low current density ($j < 0.1\text{ }\mu\text{A cm}^{-2}$) is due to the fact that the cathodic material corresponds to the highly resistive $\gamma\text{-In}_2\text{Se}_3$ phase.

Thin cells grown by a flash evaporation technique (cell B) have the same structure. Figure 4 shows a schematic representation of microbatteries having an area of 1 cm^2 and a cathode mass of $1.5\text{ - }8\text{ mg}$. The film characteristics have been reported previously [10, 11] and these studies have shown that InSe polycrystalline films obtained with a substrate temperature of $160\text{ }^\circ\text{C}$ have a Hall mobility of the order of $20\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ and a relatively high conductivity after a thermal annealing at $200\text{ }^\circ\text{C}$ for 10 h.

The electrolyte film was prepared by a quasi-flash evaporation of the lithium borate glass $\text{B}_2\text{O}_3\text{-}0.5\text{Li}_2\text{O}\text{-}0.1\text{Li}_2\text{SO}_4$, heated at $1000\text{ - }1200\text{ }^\circ\text{C}$ for a very short time. The ionic conductivity of the films was determined by the complex impedance method using two gold electrodes. A conductivity of about $10^{-8}\text{ }\Omega^{-1}\text{ cm}^{-1}$ at room temperature and an activation energy of 0.74 eV were deduced from these measurements.

Discharge and charge curves for cell (B) are shown in Fig. 5. The open circuit voltage is about 2 V and a prompt drop in voltage in the initial stage is due to ohmic polarization. A gradual decrease, due to discharge, follows. This cell shows an average voltage of 1.6 V , giving a practical capacity of $Q = 38\text{ }\mu\text{A h}$, corresponding to a volume capacity of 57 A h l^{-1} .

These results indicate that the discharge curve of the micro-solid-state battery studied is similar to that of a film cell using a non-aqueous electrolyte. However, the average voltage is slightly lower, and the charge curve shows that the capacity is reduced with cycling, even at the low ratios employed in these studies. It seems that in spite of the open structure of the cathode thin film, the ionic diffusivity is one of the important limiting factors in such cells. Considering the discharge curve shown in Fig. 5, we can assume that the discharge mechanism is a classical intercalation process. Because the charge curve shows an important overvoltage, we can imagine

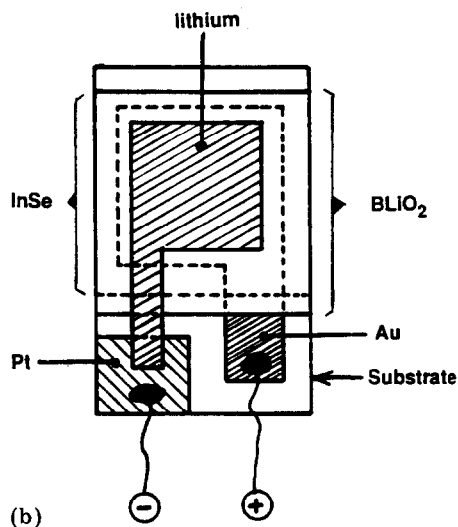
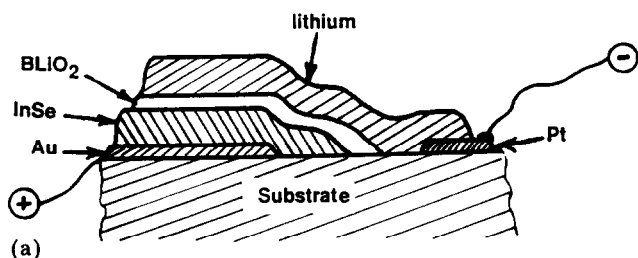


Fig. 4. (a) Schematic diagram of the lithium microbattery; (b) plan view of the lithium microbattery obtained by flash evaporation.

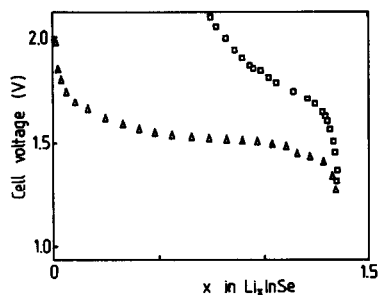


Fig. 5. Discharge-charge curves of an Li/InSe microbattery.

that in this quasi-amorphous cathode, a large number of defects are created and the de-intercalation proceeds with lithium atoms remaining in the host disordered lattice.

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