Organoindium Precursor Purification by New Sorbents Based on Titanium and Zirconium Phosphates

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ABSTRACT: High purity requirements for organometallic precursors have recently become critical in the field of III–V semiconductor films obtained by chemical vapour deposition techniques. Traditional purification routes employing physical methods need to be replaced by ones which are more rapid and effective. Such a route is described in this paper. This involves the elimination of any traces of impurity by applying several combinations of sorbents. In this way, complete elimination of lithium impurities introduced during precursor synthesis has been achieved by the use of titanium or zirconium phosphate sorbents (usually used as acidic ion exchangers in aqueous media). The method also preserves the stability of the organoindium precursor which is normally extremely sensitive to moisture. A possible explanation for these observations is given.

INTRODUCTION

Alkylindium derivatives have a variety of applications in modern microelectronics and semiconductor industries. To obtain high quality films on modern equipment [e.g. on Metallo-Organic Vapour Phase Epitaxy (MOVPE) instruments], such compounds must satisfy certain specific requirements. Of these, a very high purity is of vital importance since organic and inorganic contaminants introduced during precursor synthesis could lead to a significant deterioration in the quality of the semiconductor because of the incorporation of pyrocarbon and electrically active elements in its structure.

The present work concentrates on *N,N*-dimethylamidodiethylindium (Et$_2$InNMe$_2$) which has been tested by Italian colleagues as an alternative liquid precursor to Me$_3$In and Et$_3$In in MOVPE deposition of InP and InAs nanostructures for optoelectronics. This compound has been synthesized in the past from organolithium and organomagnesium reagents (Porchia *et al.* 1992) and hence possible contamination by the two metals involved is a problem in precursor purification.

Sorption is one of the most widespread physicochemical methods employed for the purification of liquids and solutions. However, this method has not been used for the purification of organometallic precursors for several reasons (Grafova *et al.* 1994). Traditionally, activated carbons have been applied in organic media for the separation of low molecular weight substances from those of higher molecular weight. Various types of ion-exchange resin have also been applied for the extraction of organic or inorganic compounds from aqueous solutions (Grafova *et al.* 1992).

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In our case, the problem encountered was the purification of a less polar precursor in a non-polar solvent from more polar contaminants of lower molecular weight. For such a separation, inorganic sorbents have several advantages over organic ones. Thus, the percentage of impurities introduced in their manufacture is far less and they can be readily dehydrated at moderate temperatures due to an absence of swelling properties. In our case, we have employed new inorganic cation-exchange materials based on titanium and zirconium phosphates for the ultrapurification of N,N-dimethylamidodiethylindium. Such phosphates were prepared at the Institute for Sorption and Problems of Endoecology in Kiev and have been widely used in Ukraine for the elimination of heavy metals and radionuclides which diffused after the Chernobyl accident (Bortun *et al.* 1991; Strelko *et al.* 1991).

EXPERIMENTAL

All syntheses, purifications and weighings were carried out in nitrogen-filled dry boxes (Braun). All solvents were purchased from Aldrich (Milwaukee, WI, USA). Lithium (as a 25 wt. % dispersion in mineral oil), indium(III) chloride, lithium dimethylamide and 70% doubly distilled nitric acid were used as supplied. Bromoethane was purified by reflux over fused $CaCl_2$ followed by distillation. Activated carbon was dried in vacuo at 100°C. All solvents were purified by refluxing over potassium benzophenone followed by distillation. The titanium and zirconium phosphates were prepared at the ISEP-NASU (Kiev, Ukraine) as described below.

Synthesis of N,N-dimethylamidodiethylindium

This compound had previously been synthesized at ICTIMA-CNR, Padua, Italy using EtMgCl and $LiNMe_2$ (Porchia *et al.* 1992). Two types of impurities (Li and Mg) were introduced by this method and hence the purification of the final product was long and complicated. We have replaced EtMgCl with LiC_2H_5 prepared according to a well-known method (Bryce-Smith and Turner 1953) and thereby eliminated the possibility of magnesium impurities:

$$InCl_3 + 2LiC_2H_5 = In(C_2H_5)_2Cl + 2LiCl$$
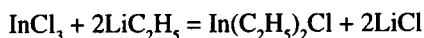
The method of Porchia *et al.* was also slightly modified to accommodate the new reagent employed and this, in turn, has led to an enhanced yield of $In(C_2H_5)_2Cl$. Thus, 2.210 g (10 mmol) of $InCl_3$ were suspended in 40 ml of benzene and a solution of LiC_2H_5 (0.72 g, 20 mmol) in 20 ml of benzene added slowly in a dropwise fashion over a period of 2 h under constant stirring and reflux which was maintained for 24 h. The fine precipitate of LiCl generated was separated by filtration and the solvent removed in vacuo to generate white crystals of $In(C_2H_5)_2Cl$ (1.79 g). The yield of 86% was significantly higher than that reported for the original synthesis.

Preparation of titanium and zirconium phosphate sorbents

Granulated spherical forms of these sorbents were obtained by the use of sol–gel technology (Strelko 1983). Thus, a 5 M solution of H_3PO_4 and a 1 M solution of $TiCl_4$ or $ZrOCl_2$ (the latter additionally containing 0.5–1 mol/l of H_2O_2) were frozen at a temperature within the range –5°C to 0°C and fed into a mixer at a volume ratio of [Ti]/[P] = 1:0.9–1.0. After thorough mixing, the reaction mix was dispersed into a granulator (a vertical column) filled with an organic solvent. The granules of hydrogel thus generated were washed with distilled water and dried at 20–100°C. The final mate-

rial, whose granules were 0.3–2 mm in dimension, had a glassy transparent appearance. Its composition may be described by the formula $Ti_{20}O_{10}(HPO_4)_{15}(H_2PO_4)_3(OH)_{27} \cdot 52.5H_2O$ (Bortun *et al.* 1995).

Preliminary drying of such sorbents in the H-form was effected at 60°C over a period of 24 h. The dried materials were stored in a dry box and subsequent to further use were additionally dried in vacuo at 60°C for 6 h. The granules were then immersed in n-hexane, i.e. the solvent chosen for purification of the Et_2InNMe_2 precursor, and maintained under such conditions until required further.

Purification of Et_2InNMe_2

The sorbent, purified as above, was added to a solution of Et_2InNMe_2 in n-hexane and allowed to stand for 2 h with occasional shaking of the flask. After this time, the sorbent was separated by filtration and the hexane solvent evaporated in vacuo.

To perform more efficient purification of the precursor, i.e. to remove organic impurities and colloidal particles, a separate portion of Et_2InNMe_2 treated as above was additionally passed through a layer of activated carbon.

Assay of samples

A quantity of untreated Et_2InNMe_2 (ca. 70 mg) was weighed accurately and transferred out of the dry box. Then, using a suitable micropipette, 1 ml of impurity-free conc. HNO_3 was added. Upon complete dissolution, 10 ml of doubly distilled water was added to the resulting solution and the preparation analyzed by atomic absorption spectroscopy.

The same procedure was adopted for each of the samples subjected to treatment by the inorganic sorbents employed, after treatment with activated carbon and after treatment with a combination of inorganic sorbent and activated carbon. The relative sensitivity of atomic absorption spectroscopy towards the possible cations present in the various samples is listed in Table 1 (Price 1983).

The analytical data obtained are summarized in Table 2. The minimum detectable amounts in the assay preparations were 5.5 ng Li^+ and 365 ng Ti^{4+}, respectively.

TABLE 1. Relative Sensitivity of Atomic Absorption Analysis

Element	Method	
	Furnace (ppb)	Flame (ppm)
Lithium	0.5	0.02
Titanium	33	1.2
Zirconium	–	8.0

TABLE 2. Effectiveness of Sorption Purification of Et_2InNMe_2 Precursor

| Sorbent	Li content (ppm)	Ti content (ppm)
Crude product	1053.3	–
Zirconium phosphate	901.4	–
Titanium phosphate	389.3	–
Activated carbon (twice)	65.0	–
Zirconium phosphate + activated carbon	non-detectable (< 0.079)	–
Titanium phosphate + activated carbon	non-detectable (< 0.079)	non-detectable (< 5.2)

RESULTS AND DISCUSSION

The main purpose of the present work was the synthesis of the precursor, Et_2InNMe_2, from commercial starting materials and the purification of the resulting material by sorption methods to ultrapure conditions (the sum of the impurities present being $\ll 10$ ppm) as required for modern MOVPE equipment. Of the reagents employed, lithium dimethylamide as supplied was only 95% pure (Aldrich 1995) and could not be purified further either by sublimation or recrystallization. A major part of the impurities present in the crude precursor was derived from this reagent. This is demonstrated by the ^1H NMR spectrum of crude Et_2InNMe_2 depicted in Figure 1(a), where the intense broad peaks visible at 2.7–2.8 ppm and at ca. 1.5 ppm may be associated with the presence of $LiNMe_2$ as an impurity. Treatment of the crude Et_2InNMe_2 with the combination of sorbents employed in this work led to a final product exhibiting signals at δ 2.469 (s, 6H); 1.445 (t, 6H); 0.754 (4, 4H) ppm [Figure 1(b)] which are characteristic of the pure precursor.

To remove such impurities, the use of inorganic phosphate-containing sorbents has been employed for the first time. These sorbents possess a selectivity towards the Li^+ ion (Bortun *et al.* 1986; Bortun and Khainakov 1990) and show good results in extraction from aqueous media where they exhibit ion-exchange properties. In experiments aimed at removing organolithium impurities from Et_2InNMe_2 in a non-aqueous non-polar organic solvent (n-hexane), it has been found that water was removed completely from the surface of the sorbent employed. Thus, water bonded to the internal structure of the sorbent was incapable of penetrating the organic medium, thereby avoiding reaction with the organoindium precursor which is extremely sensitive to moisture. Furthermore, the precursor (which normally reacts readily with H^+ ions) underwent no ion exchange in the presence of sorbent containing 3–6 mg/equiv. of H^+ ions forming part of the macromolecular structure of the material (Bortun and Khainakov 1990).

Earlier SEM studies by Grafova *et al.* (1994) showed that titanium and zirconium phosphate sorbents of the type used in the present work have a graded structure in which the functional groups on the dehydrated surface of the granules are incapable of dissociation. Hence, ion-exchange adsorption with such materials is impossible and the removal of more-polar organolithium compounds from a solution containing a great excess of less-polar organoindium precursor can only be achieved by selective molecular adsorption. In this case, the selectivity of such materials is governed by the following factors:

- steric reasons, as established previously for the affinity for Li^+ ions exhibited by titanium and zirconium phosphates. Thus Belyakov (1991) has shown that the dimensions of the electron-
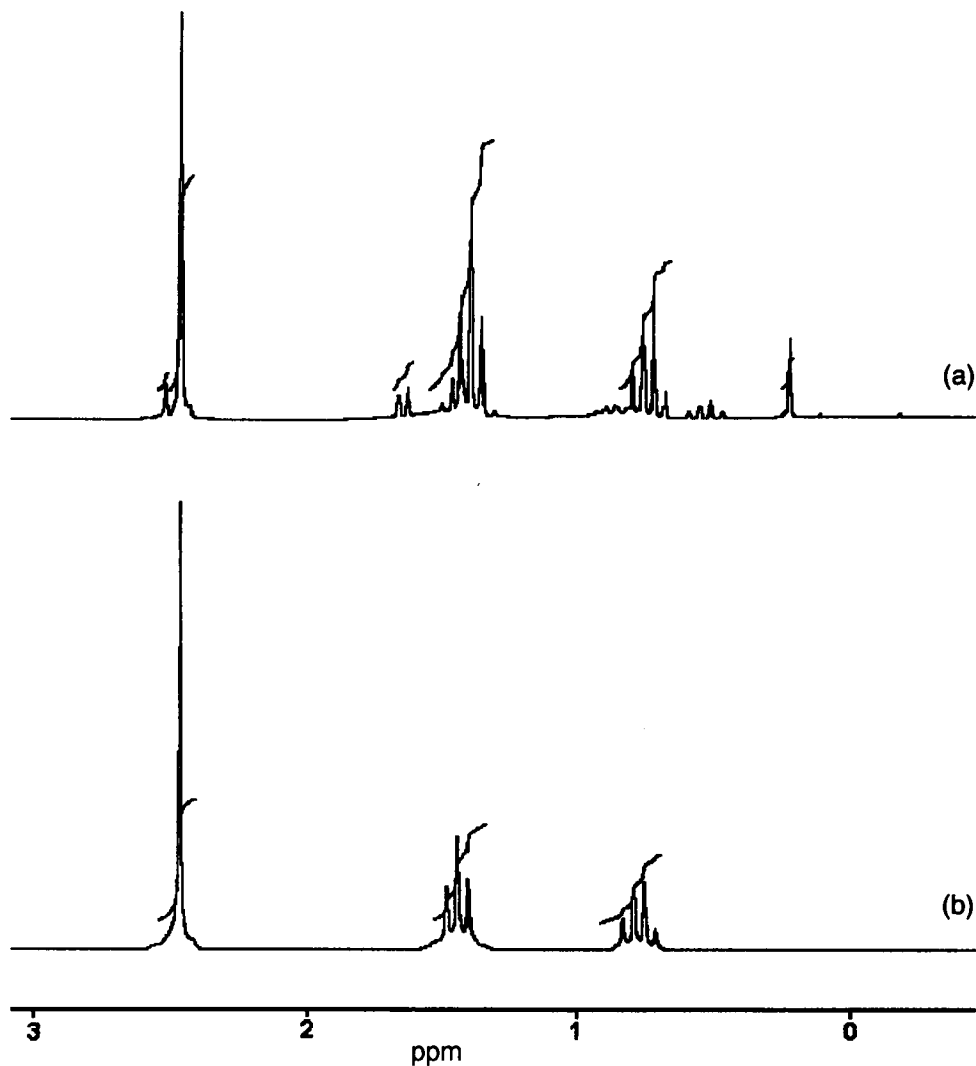
Figure 1. ¹H NMR spectra of *N,N*-dimethylamidodiethylindium: (a) crude product; (b) after purification by a combination of sorbents.

donor cavities on the surface of such sorbents are similar to those for the Li^+ ion. Furthermore, SEM studies (Grafova *et al.* 1994) have shown that the well-developed macroporous surface of these materials when dry have mean diameters of 70–90 nm, thereby creating favourable conditions for the sorption of small organolithium molecules present as impurities in the Et_2InNMe_2 precursor;

• solvent polarity, leading to the creation of favourable conditions for dipole–dipole sorbent/sorbate interactions involving more polar organolithium molecules at the expense of organoindium ones; and

• solubility factors, which allow the possible deposition of insoluble lithium phosphates in the macropores of the sorbent (Belyakov 1991).
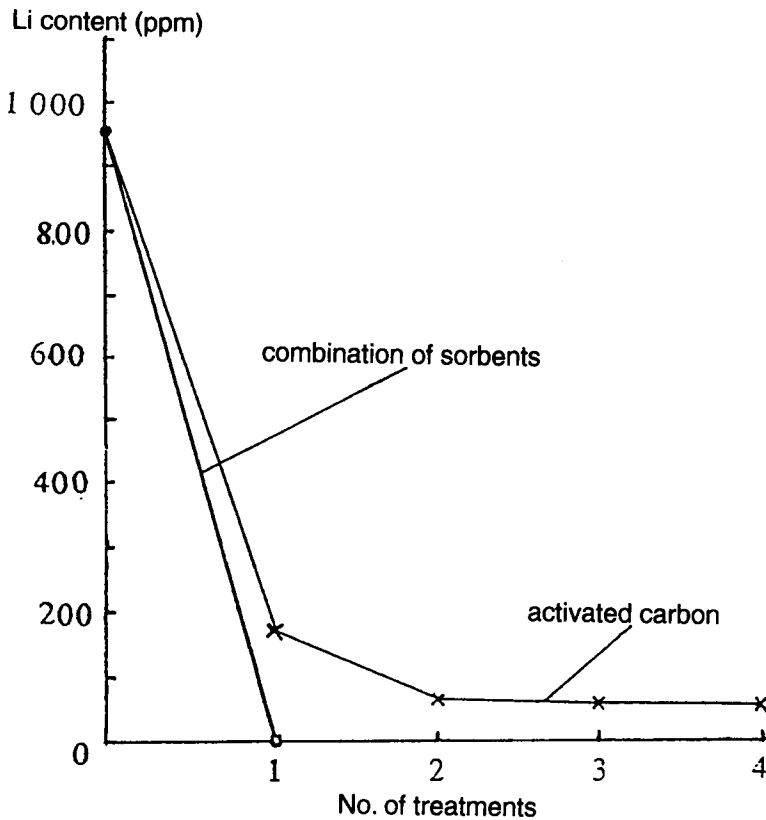
Figure 2. Lithium content in precursor after repeated treatment by activated carbon or one treatment by a combination of sorbents.

As is evident from the data listed in Table 2, it was not possible to attain the degree of purity sought for the precursor by employing phosphate sorbents alone. Thus, the use of zirconium phosphate alone led to a decrease in the Li^+ ion content of the crude precursor from 1053.3 ppm to 901.4 ppm, i.e. a decrease of ca. 14%. Similarly, the use of titanium phosphate alone, although more successful than zirconium phosphate, was only capable of reducing the Li^+ ion content by 63%. It is possible that such limited success is associated with the presence of colloidal particles in the solution which are not detained by the granulated sorbents. Normally, activated carbon is more successful at retaining such particles, but even when this material was employed successively a number of times ca. 6% of Li^+ ion impurity still remained in the precursor material (see Figure 2).

In fact, in order to attain a satisfactory level of purity (<<10 ppm impurity content) it was found necessary to involve a combination of two sorbent treatments, i.e. one based either on titanium or zirconium phosphate followed by a second based on activated carbon (see data listed in Table 2). This allowed the ultrapurification of *N,N*-dimethylamidodiethylindium to a degree suitable for the deposition of III–V semiconductor films of high quality.

CONCLUSIONS

The present work has demonstrated for the first time the satisfactory use of inorganic phosphate sorbents for the ultrapurification of organometallic precursors suitable for use in MOVPE techniques. The extension of the simple and effective purification developed opens new perspectives for the preparation of advanced materials by MOVPE (MOCVD) methods.

ACKNOWLEDGEMENTS

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