

[54]	<b>METHOD FOR VAPOR-PHASE GROWTH OF THIN FILMS OF LITHIUM NIOBATE</b>	3,047,424	7/1962	Suchoff.....	117/169 R
		3,649,501	3/1972	Sadagopan.....	204/192

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[21] Appl. No.: **430,211**

[52] **U.S. Cl.** ..... **427/248;** 427/100; 427/162;  
 427/164; 427/377

[51] **Int. Cl.<sup>2</sup>**..... **C23C 11/08**

[58] **Field of Search**..... 117/62, 107.2 R, 160 R,  
 117/225, 223, 169 R, 106 R

[57] **ABSTRACT**

A film of lithium niobate is formed on a substrate by vaporizing a lithium compound, vaporizing a niobium compound, and bringing the resultant vapors in contact with the heated substrate in an oxidizing atmosphere.

[56] **References Cited**

**UNITED STATES PATENTS**

3,018,194 1/1962 Norman et al. .... 117/107.2 R

**15 Claims, 2 Drawing Figures**

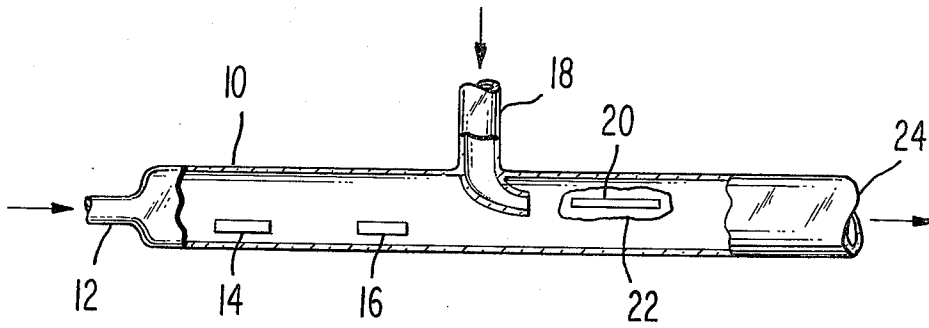


Fig. 1.

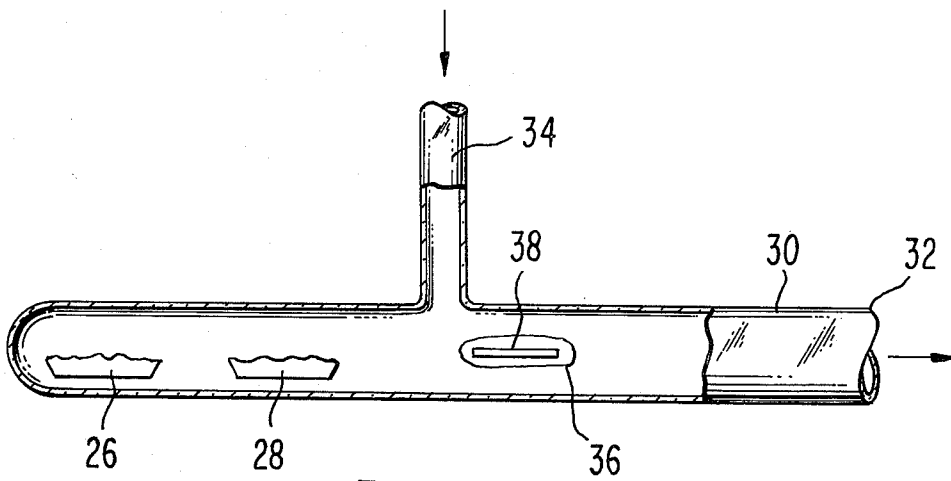


Fig. 2.

## METHOD FOR VAPOR-PHASE GROWTH OF THIN FILMS OF LITHIUM NIOBATE

### FIELD OF THE INVENTION

This invention relates to a method for depositing a film of lithium niobate on a substrate by chemical vapor deposition. More particularly, this invention relates to the vapor phase deposition of lithium niobate from volatile lithium compounds and volatile niobium compounds.

### BACKGROUND OF THE INVENTION

It is well known that lithium niobate ( $\text{LiNbO}_3$ ) is an excellent piezoelectric, electro-optic and nonlinear optic material. Several techniques for the deposition of  $\text{LiNbO}_3$  films have been tried with varying success.

A successful technique for the deposition of  $\text{LiNbO}_3$  is sputtering. Foster, *J. of Appl. Phys.*, 40 420 (1969) discloses the deposition of a  $\text{LiNbO}_3$  film by triode sputtering in an argon-oxygen gas mixture containing 5-10% oxygen. Fused quartz or sapphire substrates covered with thin layers of chrome and gold were utilized. Using a lithium niobate cathode and substrate temperatures between  $100^\circ$  and  $325^\circ$  C, both polycrystalline and oriented films of lithium niobate were produced.

U.S. Pat. No. 3,649,501 discloses a method of radio-frequency sputtering thin, single crystal films of lithium niobate. The sputtering process was carried out at substrate temperatures in a range of  $450^\circ$  C to  $870^\circ$  C in an argon atmosphere.

Miyazawa, *App. Phys. Lett.*, 23 199 (1973) describes a method for growing single crystal films of  $\text{LiNbO}_3$  on a  $\text{LiTaO}_3$  substrate by an epitaxial-growth-by-melting (EGM) method.

K. K. Winslow, et al., *Tech. Rept. RADC-TR-67-635*, 1 (1968) reports repeated failures in attempts to deposit  $\text{LiNbO}_3$  by direct vacuum evaporation. They encountered a continuing problem of dissociation of the  $\text{LiNbO}_3$  when the  $\text{LiNbO}_3$  was heated to its evaporation temperature.

A disadvantage of sputtering a  $\text{LiNbO}_3$  film is that the growth temperature of the film is limited since the sticking coefficient of the particles incident on the substrate decreases with increasing substrate temperature. Also, controlled doping of the deposited film can be difficult. Chemical vapor deposition (CVD) is a standard technique used to grow films at temperatures above those normally used in sputtering. With CVD it is possible to obtain better crystal quality than that obtainable by sputtering due to the increased surface mobility of the deposited species at high temperatures. To date there has been no report of a successful deposition of a film of  $\text{LiNbO}_3$  by CVD.

The instant process is a method for chemical vapor deposition of  $\text{LiNbO}_3$  which overcomes the problems encountered in the prior art.

### SUMMARY OF THE INVENTION

It has been discovered that thin, uniform, transparent, electro-optic films of lithium niobate can be deposited on a substrate by vaporizing a volatile lithium compound, vaporizing a volatile niobium compound and contacting the substrate with the resultant vapors in the presence of an oxidizing atmosphere at an elevated temperature.

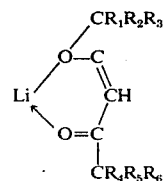
### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a sectional view of an apparatus suitable for carrying out the process of the invention.

FIG. 2 shows a sectional view of another apparatus suitable for carrying out the process of the invention.

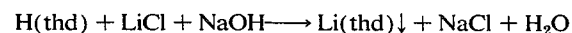
### DETAILED DESCRIPTION OF THE INVENTION

The physical properties necessary for a lithium compound to be useful in this process include a vapor pressure greater than 1 mm at a temperature of less than  $500^\circ$  C and thermal stability up to a temperature of about  $400^\circ$  C. Volatile lithium compounds useful in the present process include lithium chelates of  $\beta$ -diketones. These compounds have the general structure



where  $R_1$ - $R_6$  are selected from the group consisting of hydrogen and straight and branched chain alkyl groups.

The lithium chelate of 2,2,6,6-tetramethyl-3,5-heptanedione, hereinafter  $\text{Li}(\text{thd})$ , is particularly preferred for the present process.  $\text{Li}(\text{thd})$  is a volatile compound having a vapor pressure of about 15 mm at  $300^\circ$  C and is thermally stable up to about  $400^\circ$  C.  $\text{Li}(\text{thd})$  can be prepared by reacting the ligand, 2,2,6,6-tetramethyl-3,5-heptanedione (thd), sodium hydroxide and lithium chloride in a 50 per cent alcohol/water solution for about 3 hours, as shown by the following chemical equation:



After filtration, the  $\text{Li}(\text{thd})$  is dried and purified by vacuum sublimation.

The physical properties necessary for a niobium compound to be useful in this process include a vapor pressure greater than 1 mm at a temperature of less than  $500^\circ$  C and thermal stability up to about  $400^\circ$  C. Useful volatile niobium compounds include niobium alkoxides. Niobium methoxide is particularly preferred for this process. Niobium methoxide has a vapor pressure of 15 mm at  $200^\circ$  C and is thermally stable up to  $400^\circ$  C.

Substrates suitable for use in this process must be thermally stable up to about  $1,000^\circ$  C. Most common substrates used in electro-optic technology can be used including single crystal and polycrystalline substrates. Suitable substrates include platinum foil, yttrium aluminum garnet, spinel (orientation 111), sapphire (orientation 0001, 1124 and 1102) and lithium tantalate.

The reaction may be carried out in a wide variety of apparatus and under varying reaction conditions. A carrier gas may be used or the reaction may take place at reduced pressure. Reaction temperatures, pressures and times may be varied.

An apparatus for depositing a  $\text{LiNbO}_3$  film on a substrate is shown in FIG. 1. Referring to FIG. 1, a carrier gas is introduced into a reaction chamber 10 via an inlet 12. The carrier gas is an inert gas such as nitrogen, argon, helium, krypton, xenon, etc. A volatile niobium

compound is placed in an open container **14** in the reaction chamber **10** in the stream of the carrier gas. A volatile lithium compound is placed in an open container **16** in the reaction chamber **10** in the stream of the carrier gas. The lithium and niobium compounds are vaporized by heating the compounds to a temperature of about 100° C to 300° C.

An oxidizing gas, such as pure oxygen, is admitted into the reaction chamber **10** and into the carrier gas stream via an inlet **18**. The lithium vapor, niobium vapor and oxidizing gas are transported by the carrier gas stream to a substrate **20** placed in the reaction chamber **10**. The substrate **20** is heated to a temperature of at least about 400° C. After a reaction time from about 1 to 5 hours, a shiny black film **22** is deposited on the substrate **20**. The exhaust vapor exits from the reaction chamber **10** via an outlet **24**.

The carrier gas is then turned off and the substrate **20** and the film **22** are annealed at a temperature of about 700° to 1,000° C for 1 to 10 hours in an oxidizing atmosphere created by the continued admission of the oxidizing gas via the inlet **18**. Excess oxidizing gas and gases coming off from the film **22** exit from the reaction chamber **10** via an outlet **24**. After annealing, the film **22** formed on the substrate **20** is composed of lithium niobate.

Referring now to FIG. 2, illustrating another apparatus for performing this process, an open container **26** holding the niobium compound and an open container **28** holding the lithium compound are placed in a closed reaction chamber **30**. The reaction chamber **30** is evacuated via an outlet **32** connected to a vacuum system (not shown). After the reaction chamber **30** has been evacuated an oxidizing gas is introduced into the reaction chamber **30** via an inlet **34**. The lithium and niobium compounds are vaporized by heating the compounds to a temperature of about 100° to 300° C. The lithium vapors and the niobium vapors react at the surface of a substrate **36**. The substrate **36** is heated to a temperature of at least about 400° C. After a time of about 1 to 5 hours a thin film **38** of LiNbO<sub>3</sub> is formed on the substrate **36**.

The lithium niobate film may be doped with other metals, such as iron, by vaporizing a suitable volatile compound of the desired metal, such as Fe(thd)<sub>3</sub>, in the reaction chamber concurrently with the vaporization of the lithium and niobium compounds.

The invention will be further illustrated by the following examples, but it is to be understood that the invention is not meant to be limited to the details described therein.

#### EXAMPLE 1

A single crystal of lithium tantalate (LiTaO<sub>3</sub>) was coated with a thin film of LiNbO<sub>3</sub> in an apparatus as shown in FIG. 1. An argon carrier gas flowing at a rate of 1,900 cc/minute was passed over a container of lithium 2,2,6,6-tetramethyl-3,5-heptanedione and a container of niobium methoxide (Nb(OMe)<sub>5</sub>). The Nb(OMe)<sub>5</sub> and the Li(thd) were volatilized by heating their containers to 200° C and 300° C respectively. Oxygen gas was added to the gas mixture at a rate of 10 cc/minute. The substrate was heated to 450° C. After reacting the substrate with the gas mixture for 2 hours, a black film formed on the substrate. Without removing the substrate from the furnace, the argon carrier gas was turned off and the film on the substrate was an-

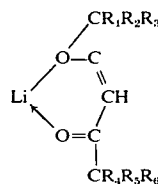
nealed in pure oxygen at 900° C. After 4 hours the black film formed a single crystal of lithium niobate which was aligned with the LiTaO<sub>3</sub> crystal.

#### EXAMPLE 2

A single crystal sapphire substrate was coated with a film of LiNbO<sub>3</sub> in an apparatus as shown in FIG. 2. The reaction chamber was placed in a multi-zone furnace. The reaction chamber was evacuated to a pressure of 5 × 10<sup>-2</sup> mm. Lithium 2,2,6,6-tetramethyl-3,5-heptanedione was vaporized by heating it to 200° C. Niobium methoxide was vaporized by heating it to 220° C. Oxygen at a pressure of 3 mm was introduced into the reaction chamber. The substrate was heated to 700° C. After 20 hours a 5 micron thick film of LiNbO<sub>3</sub> formed on the sapphire substrate surface.

What is claimed is:

1. A process of depositing a film of lithium niobate on a substrate, said substrate being thermally stable up to about 1,000°C, which comprises:
  - a. vaporizing a lithium compound having a vapor pressure greater than 1 millimeter at a temperature of less than 500°C and a stable gas phase up to 400°C,
  - b. vaporizing a niobium compound having a vapor pressure greater than 1 millimeter at a temperature of less than 500°C and a stable gas phase up to 400°C, and
  - c. contacting said substrate with the vapor of said lithium compound and the vapor of said niobium compound in an oxidizing atmosphere at a temperature of at least about 400°C.
2. A process according to claim 1 wherein the lithium compound is an organolithium compound.
3. A process according to claim 2 wherein the organolithium compound is a lithium chelate of a β-diketone of the formula



where R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub> and R<sub>6</sub> independently are selected from the group consisting of hydrogen and straight and branched chain alkyl groups.

4. A process according to claim 3 wherein the lithium chelate is the lithium chelate of 2,2,6,6-tetramethyl-3,5-heptanedione.
5. A process according to claim 1, wherein the niobium compound is an organoniobium compound.
6. A process according to claim 5 wherein the organoniobium compound is a niobium alkoxide.
7. A process according to claim 6 wherein the niobium alkoxide is niobium methoxide.
8. A process according to claim 3 wherein the lithium chelate is vaporized by heating the chelate to a temperature of between about 100° to 300° C.
9. A process according to claim 6 wherein the niobium alkoxide is vaporized by heating the niobium alkoxide to a temperature of between about 100° to 300° C.

10. A process according to claim 1 wherein the substrate is annealed in an oxidizing atmosphere at a temperature of between about 700° to 1,000° C for a period of time of between about 1 to 10 hours after contact with the lithium compound vapor and the niobium compound vapor.

11. A process according to claim 1 wherein the lithium compound vapor and the niobium compound vapor are transported to the substrate in a stream of an inert carrier gas.

12. A process according to claim 1 wherein the oxidizing atmosphere is obtained by an oxygen-containing gas.

13. A process according to claim 1 wherein the process is carried out in an evacuated chamber.

14. A process of depositing a film of lithium niobate on a substrate, said substrate being thermally stable up to about 1,000°C, which comprises:

a. vaporizing the lithium chelate of 2,2,6,6-tetramethyl-3,5-heptanedione at a temperature of from about 100° to 300° C in a stream of an inert carrier gas,

b. vaporizing niobium methoxide at a temperature of from about 100° C to 300° C,

c. heating the substrate to a temperature of at least about 400° C,

d. contacting the lithium chelate vapor and the niobium methoxide vapor with the substrate in an oxidizing atmosphere so as to deposit a film on the substrate, and

e. annealing the substrate and the deposited film at a temperature of about 700° to 1,000° C for a time of about 1 to 10 hours in an oxidizing atmosphere.

15. A process of depositing a film of lithium niobate on a substrate, said substrate being thermally stable up to about 1,000°C, in an evacuated chamber which comprises:

a. vaporizing the lithium chelate of 2,2,6,6-tetramethyl-3,5-heptanedione at a temperature of from about 100° to 300° C,

b. vaporizing niobium methoxide at a temperature of from about 100° to 300° C,

c. heating the substrate to a temperature of at least 400° C, and

d. contacting the substrate with the lithium chelate vapor and the niobium methoxide vapor in an oxidizing atmosphere for about 1 to 20 hours.

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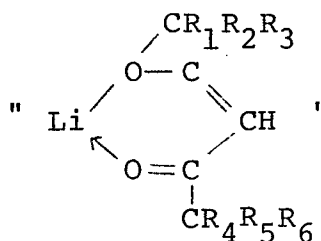
UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

PATENT NO. : 3,911,176  
DATED : October 7, 1975  
INVENTOR(S) : Bernard John Curtis et al.

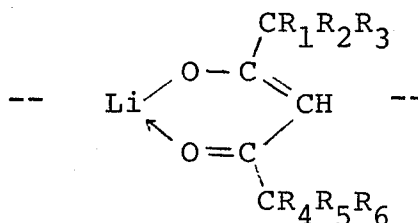
It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 20, and  
Column 4, line 40,

change



to



Column 2, line 57

change "110 $\bar{2}$ " to -- 11 $\bar{0}$ 2 ---.

Signed and Sealed this

tenth Day of February 1976

[SEAL]

Attest:

RUTH C. MASON  
Attesting Officer

C. MARSHALL DANN  
Commissioner of Patents and Trademarks