

An electromechanical responsive filmTechnical Field

The present invention relates to an electromechanical responsive film and a device
5 comprising the film.

Background

Materials with large electromechanical response, including those with electromechanical
properties, are widely used for sensors, actuators, and ultrasonic transducers. Despite
the dominance of lead-based electromechanical materials, such as lead zirconate
10 titanate (PZT), for over six decades, concerns about the toxic lead hazard have led to
increased regulatory restrictions on their uses. This has led to the development of lead-
free alternatives.

Lead-free materials with electromechanical properties comparable to PZT include
potassium sodium niobate (KNN) and alkali-deficient niobate materials due to their high
15 piezoelectric coefficient and high Curie temperature. However, the high volatility and
mobility of the alkali elements comprised in the materials significantly increase the
complexity of precisely controlling the material composition.

There is therefore a need for an improved lead-free material with electromechanical
properties.

Summary of the invention

20 The present invention seeks to address these problems, and/or to provide an improved
electromechanical responsive material.

According to a first aspect, there is provided an electromechanical responsive film
comprising an oxide of niobium having formula NbO_x , wherein $2.3 \leq x < 2.5$, the film
25 having an effective longitudinal piezoelectric strain coefficient ($d_{33, \text{eff}}$) of $\geq 50 \text{ pm/V}$.

According to a particular aspect, the oxide of niobium comprised in the film has a non-
stoichiometric composition.

The oxide of niobium comprised in the film may comprise a mixture of crystalline NbO_x
phases. In particular, the film may comprise a mixture of at least two crystalline NbO_x
30 phases. For example, the mixture of at least two crystalline NbO_x phases may be, but

not limited to, T-NbO_x and B-NbO_x. Even more in particular, the mixture of at least two crystalline NbO_x phases may further comprises TT-NbO_x.

The film may have a suitable thickness. For example, the film may have a thickness of 50-2000 nm.

- 5 According to a second aspect, there is provided an electromechanical device comprising the electromechanical responsive film according to the first aspect.

According to a particular aspect, the device may comprise a substrate and the electromechanical responsive film may be provided on the substrate. The device may further comprise at least two electrodes, wherein the electromechanical responsive film
10 may be sandwiched between the at least two electrodes.

According to another aspect, there is provided a method of forming an electromechanical responsive film comprising an oxide of niobium having formula NbO_x, wherein $2.3 \leq x < 2.5$, and having an effective longitudinal piezoelectric strain coefficient ($d_{33,i}$) of ≥ 50 pm/V, the method comprising:

- 15 - depositing niobium on a substrate surface; and
 - flowing oxygen over the substrate surface to form the electromechanical responsive film.

According to a particular aspect, the depositing may comprise sputtering niobium on the
20 substrate surface. For example, the depositing may comprise pulsed DC sputtering niobium on the substrate surface. In particular, the depositing may comprise depositing niobium using a niobium sputtering target.

The depositing may be carried out under suitable conditions. For example, the depositing may be carried out at a temperature of 500-800°C.

- 25 The flowing oxygen over the substrate surface may comprise flowing a mixture of argon and oxygen over the substrate surface. According to a particular aspect, the flowing oxygen over the substrate surface may be carried out at a pressure of 10-25 mTorr.

Brief Description of the Drawings

In order that the invention may be fully understood and readily put into practical effect
30 there shall now be described by way of non-limitative example only exemplary

embodiments, the description being with reference to the accompanying illustrative drawings. In the drawings:

Figure 1 shows a schematic representation of an electromechanical responsive device according to one embodiment;

- 5 Figure 2 shows the X-ray diffraction (XRD) pattern of an electromechanical responsive device comprising an electromechanical responsive film according to one embodiment;

Figure 3 shows the three-dimensional (3D) plot of surface displacement of an electromechanical responsive device comprising an electromechanical responsive film according to one embodiment;

- 10 Figure 4 shows the X-ray diffraction (XRD) pattern of an electromechanical responsive device comprising an electromechanical responsive film according to one embodiment;

Figure 5 shows the three-dimensional (3D) plot of surface displacement of an electromechanical responsive device comprising an electromechanical responsive film according to one embodiment;

- 15 Figure 6 shows the X-ray diffraction (XRD) pattern of an electromechanical responsive device comprising an electromechanical responsive film according to one embodiment; and

- Figure 7 shows the three-dimensional (3D) plot of surface displacement of an electromechanical responsive device comprising an electromechanical responsive film
20 according to one embodiment.

Detailed Description

As explained above, there is a need for an improved electromechanical responsive material.

- In general terms, the present invention provides an electromechanical responsive
25 material which is free of toxic and hazardous materials, such as lead. The material may be in various forms, such as a film and may be used in various applications. In particular, the material may be capable of generating a responsive electrochemical strain with a high effective longitudinal piezoelectric strain coefficient. The material may also be

formed from a simple and controllable method, thereby enabling the material to be formed comprising a controlled composition.

According to a first aspect, there is provided an electromechanical responsive film comprising an oxide of niobium having formula NbO_x , wherein $2.3 \leq x < 2.5$, the film
5 having an effective longitudinal piezoelectric strain coefficient ($d_{33,f}$) of ≥ 50 pm/V.

The effective longitudinal piezoelectric strain coefficient ($d_{33,f}$) is defined as the ratio of induced strain to applied electric field, both along the same longitudinal direction, quantifying its ability to convert electrical field into mechanical strain. In particular, the longitudinal direction may be along axis "3" (i.e. the thickness direction for a thin film).
10 The $d_{33,f}$ may be 50-300 pm/V, 75-275 pm/V, 100-250 pm/V, 125-225 pm/V, 150-200 pm/V, 175-195 pm/V.

According to a particular aspect, the oxide of niobium comprised in the film has a non-stoichiometric composition. In particular, the oxide of niobium comprised in the film may have lattice defects. For example, the oxide of niobium has a formula NbO_x , where $2.3 \leq$
15 $x < 2.5$. In particular, x may be $2.3 \leq x \leq 2.4$. Even more in particular, the oxide of niobium may have a chemical composition of, but not limited to, $\text{NbO}_{2.33}$, $\text{NbO}_{2.38}$, $\text{NbO}_{2.39}$, or a combination thereof. The chemical composition may be determined by any suitable method. For example, the chemical composition may be determined by measuring the ratio of Nb and O elements using suitable methods such as, but not limited to, X-ray
20 photoemission spectroscopy (XPS) spectra.

The oxide of niobium comprised in the film may comprise a mixture of crystalline NbO_x phases. The crystalline phases may comprise lattice defects. In particular, the film may comprise a mixture of at least two crystalline NbO_x phases. For example, oxide of niobium comprised in the film may comprise a mixture of crystalline phases comprising
25 T- NbO_x and B- NbO_x . The mixture of crystalline NbO_x phases may further comprises TT- NbO_x . The crystalline phases may be determined by any suitable method. For example, the crystalline phases may be determined based on X-ray diffraction (XRD) patterns.

The film may have a suitable thickness. For example, the film may have a thickness of 50-2000 nm. In particular, the thickness may be 100-1500 nm, 150-1200 nm, 200-1000
30 nm, 250-950 nm, 300-900 nm, 400-800 nm, 500-700 nm, 550-600 nm. Even more in particular, the thickness may be about 150-300 nm, 200-250 nm.

According to a second aspect, there is provided an electromechanical device comprising the electromechanical responsive film according to the first aspect.

The electromechanical device may be any suitable device. For example, the electromechanical device may comprise a substrate, wherein the electrochemical responsive film is provided on a surface of the substrate. The substrate may be any suitable substrate. For example, the substrate may be, but not limited to, silicon, glass, Al_2O_3 , SrTiO_3 , LaAlO_3 , SrLaAlO_4 , MgO , or a combination thereof. In particular, the substrate may be or may comprise a silicon wafer or a silicon wafer with a silicon oxide layer.

The device may further comprise at least two electrodes, wherein the electromechanical responsive film may be sandwiched between the at least two electrodes. According to a particular embodiment, the electromechanical device may comprise a substrate, a first electrode layer on a surface of the substrate, a second electrode layer, wherein the electromechanical responsive film according to the first aspect is provided between the first electrode layer and the second electrode layer.

The first electrode layer may be formed of any suitable material. In particular, the first electrode layer may be formed of any suitable electrically conductive material such as, but not limited to, a conductive metal, conductive oxide, or a combination thereof. For example, the first electrode layer may comprise, but is not limited to, platinum, SrRuO_3 , LaNiO_3 , $(\text{La,Sr})\text{MnO}_3$, gold, molybdenum, Nb-doped SrTiO_3 , or a mixture thereof.

The second electrode layer may be formed of any suitable material. In particular, the second electrode layer may be formed of any suitable electrically conductive material such as, but not limited to, a metal. For example, the second electrode layer may comprise, but is not limited to, platinum, gold, silver, aluminium, copper, titanium nitride (TiN), indium tin oxide (ITO), or a mixture thereof.

According to a particular aspect, the substrate and the first electrode layer may comprise a crystal structure and/or lattice parameters similar to that of the electromechanical responsive film to ensure proper growth of the electromechanical responsive film.

The electromechanical responsive device may generate strain when an electric field is applied through the second electrode layer and first electrode layers since the

electromechanical responsive film is provided between the first electrode layer and the second electrode layer.

A schematic representation of an example of an electromechanical responsive device is shown in Figure 1. Figure 1 shows an electromechanical responsive device 100 comprising a substrate 102, a first electrode layer 104, an electromechanical responsive film 106 and a second electrode layer 108, in a stacked arrangement. The substrate 102, the first electrode layer 104, the electromechanical responsive film 106 and/or the second electrode layer 108 may be as described above. In particular, the electromechanical responsive film 106 may be as described above in relation to the first aspect.

According to another aspect, there is provided a method of forming an electromechanical responsive film comprising an oxide of niobium having formula NbO_x , wherein $2.3 \leq x < 2.5$, and having an effective longitudinal piezoelectric strain coefficient ($d_{33,f}$) of ≥ 50 pm/V, the method comprising:

- depositing niobium on a substrate surface; and
- flowing oxygen over the substrate surface to form the electromechanical responsive film.

The formed electromechanical responsive film may be as described above in relation to the first aspect.

The depositing may comprise depositing niobium on a substrate surface by any suitable method. For example, the depositing may comprise, but is not limited to, sputtering, pulsed laser deposition, molecular beam epitaxy, atomic layer deposition, chemical vapour deposition, or a combination thereof.

According to a particular aspect, the depositing may comprise sputtering niobium on the substrate surface. For example, the depositing may comprise pulsed DC sputtering niobium on the substrate surface. In particular, the depositing may comprise depositing niobium using a niobium sputtering target. Even more in particular, the depositing may comprise depositing niobium by high power impulse magnetron sputtering using a metal niobium sputtering target.

The depositing may be carried out under suitable conditions. The depositing may be carried out at a pre-determined temperature. For example, the depositing may be carried out at a pre-determined temperature of 500-800°C. In particular, the temperature may be 550-775°C, 600-750°C, 625-725°C, 650-700°C, 675-690°C. Even more in particular, the temperature may be 600-750°C.

The depositing may be carried out for a pre-determined period of time. For example, the depositing may be carried out for a pre-determined time of 1-300 minutes. In particular, the period of time may be 30-275 min, 60-240 min, 90-200 min, 120-180 min, 150-175 min. Even more in particular, the period of time may be 60-240 minutes.

The flowing oxygen over the substrate surface may comprise flowing a gas comprising oxygen over the substrate surface. The gas comprising oxygen may be any suitable gas. For example, the gas may be an inert gas. According to a particular aspect, the flowing oxygen over the substrate surface may comprise flowing a mixture of argon and oxygen over the substrate surface.

The flowing oxygen may be carried out under suitable conditions. For example, the flowing oxygen may be carried out at a pre-determined pressure. The pre-determined pressure may be 10-25 mTorr. In particular, the pressure may be 12-22 mTorr, 15-20 mTorr, 16-19 mTorr, 17-18 mTorr.

According to a particular embodiment, there is provided a method of forming an electromechanical responsive film. In particular, the electromechanical responsive film may be as described above in relation to the first aspect. The electromechanical responsive film may be formed on a substrate, with a first electrode layer formed on the substrate. The electromechanical responsive film may be formed from a sputtering method under suitable conditions. In particular, the sputtering may be at a temperature of 500-800°C, preferably 600-750°C, a deposition time of 1-300 min, preferably 60-240 min, and/or a sputtering power of 120-200 W. Following the sputtering using a metal niobium target, a mixture of flowing gases comprising, but not limited to, argon and oxygen may be applied over the surface of the deposited niobium from the sputtering at a pressure of 10-25 mTorr, to form the NbO_x electromechanical responsive film, where $2.3 \leq x < 2.5$.

Electromechanical responsive films with different crystallinities may be obtained when the method of forming the film is carried out under different conditions. In particular, different electromechanical responsive films may be formed depending on the conditions used resulting in different defect concentration and crystal structure of the NbO_x .

- 5 While a large electromechanical response is known in some lead-free oxides, such as alkali niobate materials, the materials have complex compositions, which typically comprise three or more elements. A large electromechanical response is not expected in a binary NbO_x film. In contrast, the electromechanical responsive films described in the present application exhibit a large effective piezoelectric coefficient of ≥ 50 pm/V at
10 1 kHz, and in some instances even ≥ 200 pm/V at 1 kHz. These films may therefore be suitable alternatives for PZT films as well as for lead-free KNN films for use in various applications such as, but not limited to, microelectromechanical system (MEMS)-based applications.

- Existing lead-free oxide materials such as KNN films contain alkali compositions. In
15 particular, the high volatility and mobility of alkali elements significantly increases the complexity of precisely controlling the material composition and producing the resulting electromechanical devices, particularly for the implementation of film material for MEMS applications. This technical issue can be solved by eliminating alkali elements, as is the case in the electromechanical responsive films described in the present application.

- 20 Having now generally described the invention, the same will be more readily understood through reference to the following examples which are provided by way of illustration, and are not intended to be limiting.

Examples

Method of forming electromechanical responsive device

- 25 A silicon substrate with a platinum layer as a first electrode layer provided on the substrate surface was utilised. An electromechanical responsive film was then formed on the platinum layer. A magnetron sputtering system was used for the deposition of the film.

- The substrate comprising the platinum layer was washed and cleaned to be free from
30 contaminants. Thereafter, the magnetron sputtering system was loaded with a 3-inch

metal niobium target. The sputtering power was set to 120-200 W and the temperature was set to 500-800°C. Upon starting the pulsed DC sputtering process, Nb was deposited on the platinum layer and the temperature range was maintained to be 500-800°C. The sputtering was carried out for 1-300 minutes.

- 5 Thereafter, a mixture of argon and oxygen gas was flowed over the surface of the deposited Nb. The flowing gases were flowed at a pressure of 10-25 mTorr throughout the process. NbO_x film was then formed, where $2.3 \leq x < 2.5$.

Once the NbO_x film was formed, the second electrode layer was formed on the film. A layer of Au was sputtered on the film surface, thereby forming an electrochemical
10 responsive device comprising a substrate, a first electrode layer, an electromechanical responsive film, and a second electrode layer.

Example 1:

An electromechanical responsive NbO_{2.38} film was formed using the method described above on a Pt layer serving as a bottom electrode on a silicon wafer, and a Au layer was
15 used as the top electrode. The NbO_{2.38} film was grown with an Ar:O₂ flow ratio of 19:2, a power of 200 W, temperature of 600-750°C, and a pressure of 16 mTorr, using a 3- inch metal niobium sputtering target. The film thickness was approximately 200 nm.

The chemical composition of NbO_{2.38} was determined by XPS. Figure 2 shows the XRD patterns for the formed film, showing the two crystalline phases in the electromechanical
20 responsive film, including mixed T-NbO_x (T is from the German Tief) and B-NbO_x (B is from the German Blätter) phases.

The electromechanical response was characterized with a laser scanning vibrometer, which measured the surface displacement due to the mechanical strain induced by the applied electrical field, as shown in Figure 3. The effective piezoelectric strain coefficient
25 d_{33,f} was above 100 pm/V, up to ~196 pm/V at 1 kHz, under an alternating current (AC) unipolar voltage with the magnitude of 2 V.

Example 2:

An electromechanical responsive NbO_{2.33} film was formed using the method described above on a Pt layer serving as a bottom electrode on a silicon wafer, and a Au layer was
30 used as the top electrode. The NbO_{2.33} film was grown with an Ar:O₂ flow ratio of 19:2, a

power of 200 W, temperature of 600-700°C, and a pressure of 15 mTorr, using a 3- inch metal niobium sputtering target. The film thickness was approximately 200 nm.

The chemical composition of $\text{NbO}_{2.33}$ was determined by XPS. Figure 4 shows the XRD patterns for the formed film, showing mixed crystalline phases in the electromechanical responsive film, including TT- NbO_x (TT is from the German Tief-Tief), T- NbO_x and B- NbO_x phases.

The electromechanical response was characterized with a laser scanning vibrometer, which measured the surface displacement due to the mechanical strain induced by the applied electrical field, as shown in Figure 5. The effective piezoelectric strain coefficient $d_{33,f}$ was ~202 pm/V at 1 kHz, under an alternating current (AC) unipolar voltage with the magnitude of 2 V.

Example 3:

An electromechanical responsive $\text{NbO}_{2.39}$ film was formed using the method described above on a Pt layer serving as a bottom electrode on a silicon wafer, and a Au layer was used as the top electrode. The $\text{NbO}_{2.39}$ film was grown with an Ar: O_2 flow ratio of 19:3, a power of 200 W, temperature of 600-700°C, and a pressure of 18 mTorr, using a 3- inch metal niobium sputtering target and high power impulse magnetron sputtering method. The film thickness was approximately 200 nm.

The chemical composition of $\text{NbO}_{2.33}$ was determined by XPS. Figure 6 shows the XRD patterns for the formed film, showing mixed crystalline phases in the electromechanical responsive film of TT- NbO_x , T- NbO_x and B- NbO_x phases.

The electromechanical response was characterized with a laser scanning vibrometer, which measured the surface displacement due to the mechanical strain induced by the applied electrical field, as shown in Figure 7. The effective piezoelectric strain coefficient $d_{33,f}$ was ~258 pm/V at 1 kHz, under an alternating current (AC) unipolar voltage with the magnitude of 2 V.

Whilst the foregoing description has described exemplary embodiments, it will be understood by those skilled in the technology concerned that many variations may be made without departing from the present invention.

Claims

1. An electromechanical responsive film comprising an oxide of niobium having formula NbO_x , wherein $2.3 \leq x < 2.5$, the film having an effective longitudinal piezoelectric strain coefficient ($d_{33,f}$) of ≥ 50 pm/V.
- 5 2. The film according to claim 1, wherein the oxide of niobium comprised in the film has a non-stoichiometric composition.
3. The film according to claim 1 or 2, wherein the oxide of niobium comprised in the
10 film comprises a mixture of at least two crystalline NbO_x phases.
4. The film according to claim 3, wherein the mixture of at least two crystalline NbO_x phases comprises T- NbO_x and B- NbO_x .
- 15 5. The film according to claim 4, wherein the mixture of at least two crystalline NbO_x phases further comprises TT- NbO_x .
6. The film according to any preceding claim, wherein the film has a thickness of 50-2000 nm.
- 20 7. An electromechanical device comprising the electromechanical responsive film according to any preceding claim.
8. The device according to claim 7, wherein the electromechanical responsive film
25 is provided on a substrate.
9. The device according to claim 7 or 8, wherein the device further comprises at least two electrodes and wherein the electromechanical responsive film is sandwiched between the at least two electrodes.
- 30 10. A method of forming an electromechanical responsive film comprising an oxide of niobium having formula NbO_x , wherein $2.3 \leq x < 2.5$, and having an effective longitudinal piezoelectric strain coefficient ($d_{33,f}$) of ≥ 50 pm/V, the method comprising:
 - depositing niobium on a substrate surface; and

- flowing oxygen over the substrate surface to form the electromechanical responsive film.

11. The method according to claim 10, wherein the depositing comprises sputtering
5 niobium on the substrate surface.
12. The method according to claim 10 or 11, wherein the depositing comprises pulse DC sputtering niobium on the substrate surface.
- 10 13. The method according to any of claims 10 to 12, wherein the depositing comprises depositing niobium using a niobium sputtering target.
14. The method according to any of claims 10 to 13, wherein the depositing is carried out at a temperature of 500-800°C.
- 15 15. The method according to any of claims 10 to 14, wherein the flowing oxygen comprises flowing a mixture of argon and oxygen over the substrate surface.
16. The method according to any of claims 10 to 15, wherein the flowing oxygen is
20 at a pressure of 10-25 mTorr.