

Description**Background of the invention**5 **Field of the invention**

The present invention relates to a semiconductor substrate having a superconducting thin film layer, more particularly, it relates to a semiconductor substrate having a superconducting thin film layer composed of a compound oxide.

10 The superconducting thin film layer of the semiconductor substrate according to the present invention can be used as a wiring material for semiconductor circuits which are built in the semiconductor substrate and for fabricating Josephson junctions for Josephson devices which is built on the semiconductor substrate.

The semiconductor substrate having a superconducting thin film layer according to the present 15 invention can be used for building electronic elements or devices such as superconducting transistors, a hot electron transistors or the like.

Description of the related art

20 One of the basic technologies for fabricating an integrated circuit on a silicon single crystal substrate is a metallization technology for forming patterned conductor lines which are used for interconnecting a variety of electronic elements which are fabricated by the other basic technology including an insulating layer forming stage, a patterning stage of the insulating layer and an impurity doping stage by means of thermal diffusion, ion implantation or the like. However, a part of the signal current passing through the conventional 25 metallic conductor lines is lost because the cross sectional area of the metallic wiring line is very fine in the case of integrated circuits which are built on the silicon substrate. Therefore, it is demanded to deliver the signal current without current loss.

It is also demanded to increase the transmission velocity of signal current on the conducting lines in addition to increase the operating velocity of the active elements and passive elements themselves in order 30 to improve the net operating velocity of the integrated circuits. However, the improvement in the transmission velocity of signal current through the conventional metallic conductor lines is limited because of the energy loss in the conducting lines. Still more, the increment in the integration degree lead to increment in power consumption owing to Joule heat which is generated in the metallic conducting lines, in other words, the degree of integration in the integrated circuit is limited. Thus, there have been strong demand to use 35 superconductors as a material for the conductor lines.

The superconductivity is a phenomenon which is explained to be a kind of phase changes of electrons under which the electric resistance become zero and the perfect diamagnetism is observed. However, the critical temperature "T_c" of superconductivity could not exceed 23.2 K of Nb₃Ge which was the the highest T_c for the past ten years, so that they have not used as a wiring material for ICs.

40 The possibility of an existence of a new type of superconducting material having much higher T_c was revealed by Bednorz and Müller, who discovered a new oxide type superconductor in 1986 [Z. Phys. B64 (1986) 189].

It had been known that certain ceramic materials of compound oxides exhibit the property of superconductivity. For example, U. S. patent No. 3,932,315 discloses Ba-Pb-Bi type compound oxide which 45 shows superconductivity and Japanese patent laid-open No. 60-173,885 discloses that Ba-Bi-Pb type compound oxides also show superconductivity. These superconductors, however, possess rather lower transition temperatures of about 10 K and hence usage of liquidized helium (boiling point of 4.2 K) as cryogen is indispensable to realize superconductivity.

The new type compound oxide superconductor discovered by Bednorz and Müller is represented by 50 [La, Sr]₂CuO₄ which is called the K₂NiF₄-type oxide having a crystal structure which is similar to known perovskite type oxides. The K₂NiF₄-type compound oxides show such higher T_c as 30 K which are extremely higher than known superconducting materials.

It was also reported that C. W. Chu et al. discovered, in the United States of America, another superconducting material so called YBCO type represented by YBa₂Cu₃O_{7-x} having the critical temperature 55 of about 90 K in February 1987. Still other type new superconducting materials which were reported recently are a compound oxide of Bi-Sr-Ca-Cu-O system and Ti-Ba-Ca-Cu-O system which exhibit such high T_c as more than 100 K and which are chemically much stable than the abovementioned YBCO type compound oxide or the like.

And hence, the possibility of utilization of high-temperature superconductors as the wiring material for the integrated circuits.

The high-temperature superconductors are also demanded in the electronic devices. A typical application of the superconductor for the electronic devices is Josephson device in which quantum efficiency is observed macroscopically when an electric current is passed through a weak junction arranged between two superconductors. The tunnel junction type Josephson device is expected to be a high-speed and low-power consuming switching device owing to smaller energy gap of the superconducting material. It is also expected to utilize the Josephson device as a high sensitive sensor or detector for sensing very weak magnetic field, microwave, radiant ray or the like since variation of electromagnetic wave or magnetic field is reflected in variation of Josephson effect and can be observed as a precise quantum phenomenon. Development of the superconducting devices such as high-speed logic units or zero power loss wiring materials is also demanded in the field of high-speed computers in which the power consumption per unit area is reaching to the upper limit of the cooling capacity with increment of the integration density in order to reduce energy consumption.

Several ideas or concepts of new devices which are constructed by a combination of semiconductor and superconductor such as a superconducting transistor or a hot electron transistor have been proposed (M. Heiblum et al. "Solid State Electronics" Vol. 24. No. 343-346, 1981), but have not yet realized in a form of actual device.

In order to realize the above-mentioned superconducting devices such as superconducting transistor or hot electron transistor, it is indispensable to prepare such a semiconductor substrate that has a homogeneously deposited superconducting layer.

The present applicant already proposed several processes for preparing the thin films of the high-T_c superconductor on oxide substrate in the following patent applications: European patent application No. 88 400268.4, No. 88 400 598.4, No. 88 401 202.2, No. 88 401 208.9, No. 88 401 320.2.

The article of M. Gurvitch and A.T. Flory issued in Appl. Phys. Lett. 51(13), 28 September 1987, pp. 1027-1029, discloses a superconducting thin film of YBa₂Cu₃O₇ deposited on various substrates such as Si. Furthermore, Jap.J. Appl. Phys., Vol. 26, N°9, September 1987, pp. L1489 - L1491, T. Aida et al. discloses a superconducting thin film of YBa₂Cu₃O_{7-x} on a (100) Si single crystal used for substrate material.

In addition, earlier European application 0 282 012 published on 14/09/1988 having the priority date of 09/03/1987 discloses a semiconductor/superconductor composite comprising a substrate made of single crystal of compound semiconductor and a thin film of oxide superconductor deposited on said substrate whereby an insulating layer is interposed between said substrate and said thin film of oxide superconductor.

The earlier European application 0 292 959 published on 30/11/88 having the priority date of 26/05/87 discloses a semiconductor/superconductor composite comprising a substrate prepared of Si and a thin film of oxide superconductor deposited on said substrate whereby an insulating layer of MgO is interposed between said substrate and said thin film of oxide superconductor.

Summary of the Invention

The present invention provides a semiconductor/superconductor composite comprising a substrate made of single crystal of compound semiconductor and a thin film of oxide superconductor deposited on said substrate, characterized in that a buffer layer being made of MgO is interposed between said substrate and said thin film of oxide superconductor selected from a group consisting of compound oxides represented by the general formulae (I), (II) and (III):



in which α stands for Ba or Sr,



in which Ln stands for a least one lanthanide element selected from a group consisting of La, Nd, Sm, Eu, Gd, Dy, Ho, Y, Er, Yb, Tm and Lu and δ is a number which satisfies a range of $0 \leq \delta < 1$, and

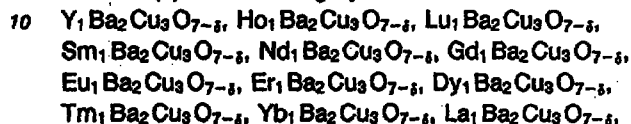


in which Θ stands for Bi or Tl, Φ stands for Sr when Θ is Bi and stands for Ba when Θ is Tl, m and n are

numbers each satisfying ranges of $6 \leq m \leq 10$ and $4 \leq n \leq 8$ respectively, $p = (6 + m + n)$, q is a number which satisfies a range of $0 < q < 1$, and r is a number which satisfies a range of $-2 \leq r \leq +2$.

The compound semiconductor material of which the substrate base is composed is preferably selected from a group comprising 3C-SiC, 6H-SiC, GaAs, GaP, InP, InSb, ZnSe, CdTe, HgCdTe, GaAlAs, GaInAs, InAlAs and InGaAsP. The substrate base is preferably composed of single crystal of these semiconductor materials.

The compound oxides having general formula (I) are considered to be composed mainly of perovskite type or oxygen deficient perovskite type crystalline structure. Namely the compound oxides having general formula (II) are following systems



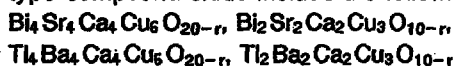
in which δ is a number which satisfies a range of $0 < \delta < 1$ and possess preferably perovskite type or quasi-perovskite type crystal structure. The term quasi-perovskite type means a structure which can be considered to have such a crystal structure that is similar to perovskite-type oxides and includes an orthorhombically distorted perovskite or a distorted oxygen-deficient perovskite or the like.

An atomic ratio of the lanthanide element "Ln":Ba:Cu is preferably 1 : 2 : 3 as is defined by the formula but the atomic ratio is not restricted strictly to this ratio. In fact, the other compound oxides having different atomic ratios which are deviate from the above-mentioned value by 10 % may exhibit superconducting property.

Still another example of the above-mentioned compound oxide is compound oxides represented by the general formula:



in which Θ stands for Bi or Tl, Φ stands for Sr when Θ is Bi and stands for Ba when Θ is Tl, m and n are numbers each satisfying ranges of $6 \leq m \leq 10$ and $4 \leq n \leq 8$ respectively, $p = (6 + m + n)$, q is a number which satisfies a range of $0 < q < 1$, and r is a number which satisfies a range of $-2 \leq r \leq +2$. Namely, this type compound oxide include the following systems:



in which r is a number which satisfies a range of $-2 \leq r \leq +2$.

When electronic systems or semiconductor devices are fabricated in the semiconductor substrate according to the present invention, the superconducting thin film layer can be removed locally by etching technique or the like so that the superconducting thin film layer is shaped into a desired pattern.

The superconducting thin film layer deposited on the semiconductor substrate according to the present invention can be used as a wiring material for semiconductor circuits which are built in the substrate base.

The semiconductor substrate according to the present invention can be used also as a substrate for fabricating an integrated circuit for building novel superconducting elements or as a substrate on which electronic devices are built. For example, Josephson junctions can be fabricated in the superconducting thin film to built Josephson devices. The semiconductor substrate according to the present invention can be used also for fabricating high-speed semiconductor devices such as superconducting transistors having more than three electrodes, superconducting FETs or hot electron transistors which utilized the interface between the superconducting thin film layer and the semiconductor substrate as is shown in Fig. 1.

Brief Description of the Drawing

Fig. 1 shows an illustrative cross sectional view of a semiconductor transistor to which the semiconductor substrate according to the present invention is applicable.

Fig. 1 shows the concept of the superconducting transistor. The superconducting transistor comprises a single crystal substrate 3 of semiconductor and a superconducting thin film layer 1 deposited on a surface of the substrate 3. Fig. 1 illustrates also the conventional insulator layers 2 and 4 and a special shape of the superconducting transistor which can be fabricated by the conventional lithography and etching technique. In this superconducting transistor, superconducting current pass through an active channel 3' of the semiconductor 3 by the "contact effect" of superconductor segments or electrodes 1' and 1'' and is controlled by a gate 5.

For example, the superconducting transistor can be fabricated as following: At first, the insulator layer 2 is formed by the conventional oxidation technique on the semiconductor substrate 3 and then is etched into a desired pattern. Then, the superconducting thin film layer 1 according to the present invention is deposited. The deposited superconducting thin film 1 is then divided into two the superconductor electrodes 1' and 1'' by ion etching technique. Another insulator layer 4 is formed on the opposite surface of the semiconductor substrate 3 which has been etched previously. A gate electrode 5 is deposited by the conventional metallization technique.

Now, we will describe a process for producing the above-mentioned semiconductor substrate according to the present invention.

The semiconductor substrate according to the present invention is prepared by depositing the superconducting thin film layer on a single crystal of semiconductor material.

The deposition of the superconducting thin film layer can be effected by physical vapour deposition (PVD) technique such as sputtering, vacuum-deposition, molecular beam epitaxy (MBE), ion beam deposition or the like or by chemical vapour deposition (CVD) technique such as thermal CVD, plasma CVD, photo CVD, MOCVD or the like. Among the physical vapour deposition (PVD) technique, magnetron sputtering is most preferable.

According to one aspect of the present invention, the deposition must be carried out under a such condition that the semiconductor substrate of single crystal is not heated higher than 700 °C. If the substrate temperature exceed 700 °C, the quality of the semiconductor single crystal is spoiled and also a reaction occur between the semiconductor material and the compound oxide of which the superconducting thin film is composed. To the contrary, if the substrate temperature is not higher than 200 °C, it is impossible or difficult to prepare the superconducting thin film having desired properties.

The superconducting thin film is preferably deposited on plane or {100} plane in order to assure orientation of crystalline structure of the superconducting thin film deposited. In fact, the superconducting thin films of the above-mentioned type compound oxides shows anisotropy in the critical current density. Namely, the current passing along a direction which is in parallel with a plane defined by a-axis and b-axis of the crystal show a very high critical current density, while the current passing along the other directions is relatively lower. Therefore, in order to match the crystalline orientation of the superconducting thin film with that of the semiconductor substrate, it is preferable to deposit the superconducting thin film on the specified plan, preferably {001} plane of the semiconductor single crystal. In the special application, it is also possible to use {110} plane. In this case, the c-axis of the superconducting thin film become in parallel with a surface of a substrate, so that current is flown perpendicularly with respect to the c-axis.

According to the present invention, a buffer layer is interposed between the superconducting thin film layer and the compound semiconductor substrate. The buffer layer is deposited on the single crystal of compound semiconductor material before the deposition of the superconducting thin film layer. The function of this buffer layer is to improve the orientation or crystallization of the superconducting thin film layer. The buffer layer is composed of MgO.

The following examples are only for technical information and are not falling within the scope of the claims.

Example 1

In this example, a buffer layer of MgO having a thickness of 500 Å is deposited on a single crystal of silicon substrate before the superconducting thin film layer is deposited.

The MgO buffer layer is deposited by sputtering technique on {100} plane of the silicon substrate which is heated at 650 °C.

Two samples are prepared by depositing two superconducting thin film layers of Y-Ba-Cu-O system and Ho-Ba-Cu-O system on the MgO buffer layer respectively. Each of two superconducting thin films is deposited by magnetron RF sputtering technique which is itself known. Targets used in the sputtering are sintered powder of $\text{YBa}_2\text{Cu}_{4.5}\text{O}_x$ for Y-Ba-Cu-O system and $\text{HoBa}_{2.2}\text{Cu}_{4.7}\text{O}_x$ for Ho-Ba-Cu-O system respectively. Special attention is paid to the distance between the substrate and the target and to the power of high-frequency, while the silicon substrate is heated at 700 °C during the sputtering operation so that superconducting thin film layers of the respective compound oxides are grown to 1,000 Å.

The resulting samples of semiconductor substrates having the superconducting thin film layer show good condition at an interface between the semiconductor substrate (MgO buffer layer) and the superconducting thin film layer. Table 1 shows the critical temperature T_{co} (a temperature where the phenomenon of superconductivity start to be observed), T_{ci} (a temperature where zero resistance is observed) and the critical current density determined at 77 K of the superconducting thin films of respective samples.

Table 1

Superconducting thin film	Critical temperature		Critical current density (A/cm ²)
	T _{co} (K)	T _{ci} (K)	
Y ₁ Ba ₂ Cu ₃ O _{7-x}	96	91	3.0 x 10 ⁵
Ho ₁ Ba ₂ Cu ₃ O _{7-x}	98	94	3.2 x 10 ⁵

Example 2

The same operation as Example 1 is repeated except that the buffer layer is not used and semiconductor substrate of silicon is replaced by respective single crystal of 3C-SiC, 6H-SiC, GaAs, GaP, InP, InSb, ZnSe, CdTe, HgCdTe, GaAlAs, GaInAs, InAlAs and InGaAsP.

For each substrate, two samples are prepared by depositing two superconducting thin film layers of Y-Ba-Cu-O system and Ho-Ba-Cu-O system on {100} plane or {110} plane by magnetron RF sputtering technique which is itself known. Targets used in the sputtering are sintered powders of YBa₂Cu_{4.5}O_x for Y-Ba-Cu-O system and HoBa_{2.2}Cu_{4.7}O_x for Ho-Ba-Cu-O system respectively. Special attention is paid to the distance between the substrate and the target and to the power of high-frequency, while the silicon substrate is heated at 700 °C during the sputtering operation so that superconducting thin film layers of the respective compound oxides are grown to 1,000 Å.

The resulting samples of semiconductor substrates having the superconducting thin film layer show good condition at an interface between the semiconductor substrate and the superconducting thin film layer. Table 2 shows the critical temperature T_{co} (a temperature where the phenomenon of superconductivity start to be observed), T_{ci} (a temperature where zero resistance is observed) and the critical current density determined at 77 K of the superconducting thin films of respective samples.

Table 2

Semiconductor single crystal	Plane deposit.	Superconducting thin film	Critical temp. (K)		Critical current density (A/cm ²)
			T _{co}	T _{ci}	
3C-SiC	100	YBaCuO (1)	96	91	3.0 x 10 ⁵
6H-SiC	0001		89	86	2.5 x 10 ⁵
GaAs	100		89	85	2.8 x 10 ⁵
GaP	110		83	80	2.2 x 10 ⁵
InP	100		84	81	2.3 x 10 ⁵
InSb	100		86	84	3.3 x 10 ⁵
ZnSe	100		87	85	2.9 x 10 ⁵
CdTe	100		87	84	3.2 x 10 ⁵
HgCdTe	100		84	81	2.9 x 10 ⁵
GaAlAs	100		87	84	2.2 x 10 ⁵
GaInAs	100		86	84	2.5 x 10 ⁵
InAlAs	100		87	85	2.1 x 10 ⁵
InGaAsP	100		82	80	2.6 x 10 ⁵
3C-SiC	100	HoBaCuO (2)	98	94	3.2 x 10 ⁵
6H-SiC	0001		92	90	3.1 x 10 ⁵
GaAs	100		88	86	3.0 x 10 ⁵
GaP	110		89	87	3.2 x 10 ⁵
InP	100		91	88	2.9 x 10 ⁵
InSb	100		84	82	3.0 x 10 ⁵
ZnSe	100		89	86	3.4 x 10 ⁵
CdTe	100		86	84	3.4 x 10 ⁵
HgCdTe	100		83	82	2.8 x 10 ⁵
GaAlAs	100		84	82	2.6 x 10 ⁵
GaInAs	100		89	86	2.8 x 10 ⁵
InAlAs	100		88	86	2.9 x 10 ⁵
InGaAsP	100		84	83	2.7 x 10 ⁵

Note:

(1) Y₁Ba₂Cu₃O_{7-x}(2) Ho₁Ba₂Cu₃O_{7-x}

Example 3

The same operation as Example 1 is repeated except that a superconducting thin film of Bi-Sr-Ca-Cu-O system is deposited on the silicon substrate in place of Y-Ba-Cu-O system in Example 1 by using a target of Bi_{1.4}Sr₁Ca₁Cu_{1.5}O_x. The resulting semiconductor substrate having the superconducting thin film layer of a compound oxide of Bi-Sr-Ca-Cu-O system on the MgO buffer layer deposited on the silicon substrate shows good condition at the interface between the MgO layer and the superconducting thin film layer. Table 3 shows the critical temperature T_{co} and T_{ci} of the superconducting thin film.

Table 3

Superconducting thin film	Critical temperature		Critical current density (A/cm ²)
	T _{co} (K)	T _{ci} (K)	
Bi _{1.4} Sr ₁ Ca ₁ Cu _{1.5} O _x	113	102	3.0 x 10 ⁴



Claims

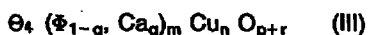
1. A semiconductor/superconductor composite comprising a substrate (3) made of single crystal of compound semiconductor and a thin film (1) of oxide superconductor deposited on said substrate (3), characterized in that a buffer layer being made of MgO is interposed between said substrate (3) and said thin film (1) of oxide superconductor selected from a group consisting of compound oxides represented by the general formulae (I), (II), (III) :



in which α stands for Ba or Sr,



in which Ln stands for at least one lanthanide element selected from a group consisting of La, Nd, Sm, Eu, Gd, Dy, Ho, Y, Er, Yb, Tm and Lu and δ is a number which satisfies a range of $0 \leq \delta < 1$, and



in which Θ stands for Bi or Tl, Φ stands for Sr when Θ is Bi and stands for Ba when Θ is Tl, m and n are numbers each satisfying ranges of $6 \leq m \leq 10$ and $4 \leq n \leq 8$ respectively, $p = (6 + m + n)$, q is a number which satisfies a range of $0 < q < 1$, and r is a number which satisfies a range of $-2 \leq r \leq +2$.

2. The semiconductor/superconductor composite set forth in claim 1, wherein said compound semiconductor is made of a material selected from the group consisting of 3C-SiC, 6H-SiC, GaAs, GaP, InP, InSb, ZnSe, CdTe, HgCdTe, GaAlAs, GaInAs, InAlAs and InGaAsP.

3. The semiconductor/superconductor composite set forth in claim 1 or 2, wherein said thin film has a crystal structure of perovskite or oxygen deficient perovskite.

Patentansprüche

1. Ein halbleitender/supraleitender Schichtkörper mit einem Substrat (3), bestehend aus einer halbleitenden Einkristallzusammensetzung und aus einem dünnen Film (1) eines supraleitenden Oxids, der auf dem Substrat (3) abgeschieden ist, dadurch gekennzeichnet, daß eine Pufferschicht aus MgO zwischen dem Substrat (3) und dem dünnen Film (1) aus supraleitendem Oxid angeordnet ist, welche aus einer Gruppe ausgewählt ist, die aus zusammengesetzten Oxiden besteht, welche durch die allgemeine Formel I, II, III dargestellt wird



wobei α für Ba oder Sr steht,



wobei Ln für wenigstens ein Lanthanidenelement steht, das ausgewählt ist aus der Gruppe, welche umfaßt La, Nd, Sm, Eu, Gd, Dy, Ho, Y, Er, Yb, Tm und Lu und δ eine Zahl im Bereich $0 \leq \delta < 1$ ist und



wobei Θ für Bi oder Tl steht, Φ für Sr steht, wenn Θ Bi ist und für Ba steht, wenn Θ Tl ist, m und n Zahlen sind, welche die Bereiche $6 \leq m \leq 10$ und $4 \leq n \leq 8$ erfüllen, $p = (6 + m + n)$ ist, q eine Zahl ist, welche den Bereich $0 < q < 1$ erfüllt und r eine Zahl ist, welche den Bereich $-2 \leq r \leq +2$ erfüllt.

2. Der halbleitende/supraleitende Schichtkörper nach Anspruch 1, bei dem die Halbleiterzusammensetzung aus einem Material besteht, das ausgewählt ist aus der Gruppe bestehend aus 3C-SiC, 6H-SiC, GaAs, GaP, InP, InSb, ZnSe, CdTe, HgCdTe, GaAlAs, GaInAs, InAlAs und InGaAsP.



3. Der halbleitende/supraleitende Schichtkörper nach Anspruch 1 oder 2, bei der der dünne Film eine Perovskitkristallstruktur oder eine Pervoskitkristallstruktur mit Sauerstofffehlstellen aufweist.

Revendications

1. Composite supraconducteur/semiconducteur comprenant un substrat (3) fait d'un composé semiconducteur monocristallin et comprenant un film mince (1) d'oxyde supraconducteur déposé sur ledit substrat (3), caractérisé en ce qu'une couche intermédiaire de MgO est intercalée entre ledit substrat (3) et ledit film mince (1) d'oxyde supraconducteur choisi parmi un groupe constitué d'oxydes composés représentés par les formules globales (I), (II) et (III) :



dans laquelle α remplace Ba ou Sr,



dans laquelle Ln remplace au moins un élément lanthanide choisi à partir d'un groupe constitué de La, Nd, Sm, Eu, Gd, Dy, Ho, Y, Er, Yb, Tm et Lu et δ est un nombre qui satisfait à la condition suivante $0 \leq \delta < 1$, et



dans laquelle Θ remplace Bi ou Tl, Φ remplace Sr lorsque Θ remplace Bi et remplace Ba lorsque Θ remplace Tl, m et n sont des nombres qui satisfont respectivement aux conditions suivantes $6 \leq m \leq 10$ et $4 \leq n \leq 8$, $p = (6+m+n)$, q est un nombre qui satisfait à la condition $0 < q < 1$, et r est un nombre qui satisfait à la condition $-2 \leq r \leq +2$.

2. Composite supraconducteur/semiconducteur selon la revendication 1, dans lequel ledit semiconducteur composé est fabriqué à partir d'un matériau choisi dans le groupe comprenant 3C-SiC, 6H-SiC, GaAs, GaP, InP, InSb, ZnSe, CdTe, HgCdTe, GaAlAs, GaInAs, InAlAs et InGaAsP.
3. Composite supraconducteur/semiconducteur selon la revendication 1 ou 2, dans lequel ledit film mince a une structure cristalline de perovskite ou de perovskite à déficit en oxygène.