Description

This invention relates to methods for making low resistance contacts to semiconductor materials and, more particularly, to methods for making ohmic contacts to III-V materials.

Background of the Invention

One of the most significant developments in semiconductor technology in recent years has been the increased use and importance of compound semiconductors, particularly the group III-V compounds composed of elements III and V of the periodic table such as gallium arsenide and indium phosphide. The band gap characteristics of III-V semiconductors make them particularly useful as photonic devices such as lasers, light emitting diodes (LEDs) and photodetectors. The high electron mobility of such materials also make them promising for the production of high speed electronic devices such as high speed integrated circuits. Photonic devices are often made by forming on the surface of the substrate a succession of epitaxial layers (an epitaxial layer is a layer of material deposited on a substrate such that it has a crystal structure that constitutes in effect an extension of the crystal structure of the substrate). For example, a laser structure based on indium gallium arsenide phosphide epitaxially grown on an indium phosphide substrate emits light in a wavelength range where absorption losses of silica based optical fibers is at a minimum. Also, modulation doped hetero structures grown on indium phosphide substrates such as $In_{0.53}Ga_{0.47}As/InP$ have been used to make high speed integrated circuit devices.

Most useful III-V semiconductor devices require a low resistance or ohmic metal contact to the III-V material for applying electrical current to, or removing electrical current from, the device. Such ohmic contacts are usually made by evaporating a thin gold film onto the semiconductor substrate. While such gold films have reasonably good electrical characteristics, they frequently do not adhere well to the substrate and are often characterized by poor uniformity, reproducibility and reliability. Many of these problems probably result largely from the fact that the gold alloys to the III-V material and then diffuses into the substrate. The papers, "On the Formation of Binary Compounds in Au/InP System," A. Piotrowska et al., *Journal of Applied Physics*, Vol. 52, No. 8, August 1981, pp. 5112-5117, and "The Migration of Gold from the p-contact as a Source of Dark Spot Defects in InP/InGaAsP LED's," A. K. Chin et al., *IEEE Transactions of Electronic Devices*, Vol. ED-30, No. 4, April 1983, pp. 304-309, document the large diffusion depth of gold into the substrate and the problems that can result. The paper, "The Design and Realization of a High Reliability Semiconductor Laser for Single-Model Fiber-Optical Communication Links," A. R. Goodwin et al., *Journal of Light Wave Technology*, Vol. 6, No. 9, September 1988, pp. 1424-1434, further documents degradation due to the electromigration of gold into the device during operation. Furthermore, as described in "Interaction Between Zinc Metallization and Indium Phosphide," S. Nakahara et al., *Solid-State Electronics*, Vol. 27, No. 6, June 1984, pp. 557-564, dopant atoms added to the contact diffuse rapidly through indium phosphide, which can result in a reduction of the ohmic behavior. A high contact resistance not only results in low efficiency and reduces the speed of such devices, but also increases the temperature of the active region leading to a higher threshold current. Another consideration in designing ohmic contact is the desirability of using a metal that can be patterned by reactive ion etching (reactive ion etching or dry etching is a well-known technique for using ions of a plasma selectively to etch metal films).

Accordingly, there has been a long-felt need for a method for making ohmic contacts to III-V semiconductor substrates that are uniform, reproducible, reliable, adhere well, do not interfere with the electrical characteristics of the semiconductor substrate, and are amenable to reactive ion etching.

Summary of the Invention

In accordance with the invention, an ohmic contact to a substrate of III-V semiconductor material comprises a thin film composed of at least tungsten and antimony. Preferably, the contact should be eighty to ninety-five percent by weight of tungsten, five to ten percent by weight of antimony and zero to fifteen percent by weight of indium. The film is preferably applied by simultaneously sputtering tungsten, antimony and indium onto the substrate in a manner that will be described in greater detail below.

Ohmic contacts in accordance with the invention do not alloy to a III-V semiconductor substrate such as indium phosphide but they nevertheless adhere well; specifically, it has been found that the presence of indium in the contact significantly aids contact adherence and reduces sheet resistance. There is very little metal diffusion into the substrate and little electromigration during operation. The contacts have been found to be uniform, reproducible, reliable, and amenable to patterning by known reactive ion etching techniques.

These and other objects, features and benefits of the invention will be better understood from a consideration of the following detailed description taken in conjunction with the accompanying drawing.

Brief Description of the Drawing

FIG. 1 is a schematic sectional view of a semiconductor diode having an ohmic contact in accor-

dance with the invention;

FIG. 2 is a schematic diagram of apparatus for sputtering metal onto a semiconductor to make ohmic contacts in accordance with the invention.

Detailed Description

The use of ohmic contacts on various semiconductor devices such as lasers, integrated circuits, photodetectors and light emitting diodes is so well known and well understood in the art that their use in these different contexts will, for the sake of brevity, not be described. Basically, an ohmic contact is one in which there is a small or no electronic barrier at the interface between the metal contact and the semiconductor, as opposed to an interface which constitutes a junction barrier or Schottky barrier. With the electronic barrier being very small, there is a small resistance to the flow of electricity across the interface. Various methods of depositing metals on semiconductors to make such contacts are well known and the following description presupposes a knowledge of such methods, some of which are exemplified in the prior art cited above.

FIG. 1 shows schematically and only for purposes of illustration a semiconductor diode 10 having a junction 11 defined at the interface between semiconductor portions 12 and 13 that are doped with p-type and n-type impurities, respectively. Metal contacts 14 and 15 are used to connect the diode to external circuitry and illustratively both of them are required to be low resistance or ohmic contacts. The semiconductor regions 12 and 13 are both of III-V semiconductor materials and the diode may be of the type which is used as a photodetector; that is, it generates electricity upon the impingement of light on junction 11. III-V semiconductor diodes, as is known in the art, can also be used as lasers, LEDs and rectifiers.

In accordance with the invention, the metal ohmic contact 14 is composed of eighty to ninety-five percent by weight of tungsten, five to ten percent by weight of antimony, and zero to fifteen percent by weight of indium. Metal contacts of this composition have been found to give extremely low resistance contact to the semiconductor. The presence of indium significantly reduces sheet resistance, and it aids adherence, but is not absolutely essential for obtaining an ohmic contact.

FIG. 2 illustrates schematically sputtering apparatus 18 that illustratively is used for applying ohmic contacts to III-V semiconductors in accordance with the invention. The sputtering apparatus 18, which has been used for demonstrating the invention, is a machine known as the CVC 601 Sputtering Machine, which is commercially available from the CVC Company of Rochester, New York. The machine includes a rotatable support 19, driven by a central axle 20, for supporting a plurality of semiconductor wafers 21. Located below the wafers are a series of targets 23, 24 and 28 which constitute sources of the metals to be applied. A tungsten target 23 and an indium target 24 are respectively connected to dc sources 25 and 26. A target 28 of antimony is connected through a matching circuit 29 to a source of radio-frequency power 30. The sputtering apparatus 18 is evacuated by a vacuum pump 32 and is further evacuated by a cryo pump 33, both of which are selectively connected to the sputtering apparatus by a valve 34. A controlled amount of argon is introduced into the apparatus from a source 35 selectively connected to the sputtering apparatus by a valve 36.

As is known in the art, the combination of vacuum pump 32 and cryo pump 33 produce a near vacuum within the sputtering apparatus 18 and argon source 35 provides a precisely controlled source of gas molecules within the apparatus. The dc sources 25 and 26 and the r-f source 30 accelerate gas molecules toward the targets 23, 24 and 28, and the collision of such molecules provides enough energy to cause molecules of the target material to be ejected. These target molecules then collect on the underside 38 of wafers 21. In accordance with the invention, all three metals are sputtered simultaneously, with the proportions of each metal sputtered being controlled through control of the power sources 25, 26 and 30.

After sputtering, the wafers 21 are preferably annealed by heating in a separate furnace. Various operations such as photolithographic masking and etching may then be used to define a number of electrical contacts from the metal film that has been coated on the wafer. In accordance with one aspect of the invention, the metal film can be cut or patterned by a known process known as reactive ion etching. Typically, the wafer is thereafter cut to form a number of individual chips which eventually constitute individual electronic devices.

In demonstrations of the invention that have been made, indium phosphide substrates were doped with either tin or zinc to give n-type or p-type doping, respectively, of 10^{18} atoms per cubic centimeter. The substrates were cleaned of surface oxide by etching in a solution of sulfuric acid and hydrogen peroxide, were then spray rinsed in deionized water and blown dry. They were mounted as shown in FIG. 2 after which the sputtering apparatus was cryo pumped to a base pressure of about $2{,}6.10^{-5}$ Pa. (2×10^{-7} torr). The antimony target was biased with 100-150 watts of r-f power during operation, and the tungsten and indium targets were biased with dc voltages of between eighty and two hundred fifty volts. The argon pressure during sputtering was held at 0,7 Pa.(five millitorr), the equivalent of about fifty standard cubic centimeters per minute, in which case the sputtering rate was typically 0,1 to 0,2mm/s (one to two angstroms per second). The substrates revolved above the targets at ten revolutions per minute with their (100) crystal-

lographic surfaces being exposed for coating. The contacts were found to be ohmic with eighty to ninety-five percent by weight of tungsten, five to ten percent by weight of antimony, and zero to fifteen percent by weight of indium. After sputtering, the samples were annealed in an argon atmosphere at a temperature of 300-450°C for between ten and thirty minutes.

As is known, the sputtering rate for dc biased targets is a function of applied dc voltage and the rate for r-f biased targets is a function of applied r-f power. A preponderance of sputtered tungsten over indium is obtained by biasing tungsten target 23 at voltages of between two hundred and two hundred fifty volts while biasing indium target 24 at voltages of between eighty and one hundred fifty volts. As is known, sputtering rate is also a function of argon pressure. If desired, one could sputter from a single target containing all three metals or one containing two metals. Pure antimony does not sputter too dependably when biased by a dc source because it has a high resistance, giving it a tendency to accumulate charge, and for this reason r-f sputtering from antimony target 28 is preferred. If combined with more conductive metals, it could easily be dc sputtered. Further, no reason is known that would in principle preclude other plating methods, such as evaporation.

The contacts that were made were found to be ohmic after annealing. Contacts made to n-type indium phosphide were ohmic prior to annealing, but p-type contacts appear to require annealing. For pattern dimensions of between fifty and two hundred fifty micrometers, the contact resistance was found to be in the range of 10^{-6} ohms per square centimeter. The sheet resistance of the films having a thickness of about 100 nanometers (one thousand angstroms) was approximately twelve ohms per square when annealed at 400°C. Microscopic examination showed that there was little or no alloying of the metal to the semiconductor. As a consequence, there was little diffusion of the metal into the semiconductor as compared with the diffusion of gold in an indium phosphide matrix under similar conditions. From these examinations, it has been inferred that the antimony of the structure provides a low band gap interfaced to the semiconductor, while indium in the metal contact minimizes out-diffusion of indium from the semiconductor substrate. Unlike alloy contacts, the solid phase reacted tungsten-indium-antimony contact retains the sharp lateral conductivity profile even after annealing at 450°C.

It is to be understood that the embodiments shown are merely illustrative of methods for practicing the invention. While sputtering is the preferred method for applying the component metals, other methods could alternatively be used. Annealing aids long-term stability and reduces contact resistance, but is not essential in obtaining ohmic contacts in n-type substrates.

Claims

1. An electronic device comprising a substrate of III-V semiconductor material and an ohmic metal contact adhered to said substrate characterized in that:
   the ohmic contact comprises a thin film composed of at least tungsten and antimony.

2. The electronic device of claim 1 further characterized in that:
   the ohmic contact comprises substantially eighty to ninety-five per cent by weight of tungsten, five to ten percent by weight of antimony, and zero to fifteen percent by weight of indium.

3. The device of claim 2 further characterized in that:
   the substrate comprises crystalline indium phosphide.

4. A method of making an electronic device comprising the steps of applying a metal film to a substrate of III-V material so as to make an ohmic contact thereto characterized in that:
   tungsten and antimony are deposited by sputtering onto the substrate so as to form the metal film.

5. The method of claim 4 further characterized in that:
   the tungsten and antimony are sputtered simultaneously.

6. The method of claim 5 further characterized in that:
   tungsten, antimony and indium are sputtered simultaneously onto the substrate to make the metal film.

7. The method of claim 6 further characterized in that:
   the sputtering of tungsten and indium is done by dc sputtering and the sputtering of antimony is done by r-f sputtering.

8. The method of claim 7 further characterized in that:
   the substrate comprises crystalline indium phosphide.

9. The method of claim 8 further characterized in that:
   approximately eighty to ninety-five percent by weight of tungsten, approximately five to ten percent by weight of antimony and approximately zero to fifteen percent by weight of indium are deposited by sputtering to form the metal film.

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lographic surfaces being exposed for coating. The contacts were found to be ohmic with eighty to ninety-five percent by weight of tungsten, five to ten percent by weight of antimony, and zero to fifteen percent by weight of indium. After sputtering, the samples were annealed in an argon atmosphere at a temperature of 300-450°C for between ten and thirty minutes.

As is known, the sputtering rate for dc biased targets is a function of applied dc voltage and the rate for r-f biased targets is a function of applied r-f power. A preponderance of sputtered tungsten over indium is obtained by biasing tungsten target 23 at voltages of between two hundred and two hundred fifty volts while biasing indium target 24 at voltages of between eighty and one hundred fifty volts. As is known, sputtering rate is also a function of argon pressure. If desired, one could sputter from a single target containing all three metals or one containing two metals. Pure antimony does not sputter too dependably when biased by a dc source because it has a high resistance, giving it a tendency to accumulate charge, and for this reason r-f sputtering from antimony target 28 is preferred. If combined with more conductive metals, it could easily be dc sputtered. Further, no reason is known that would in principle preclude other plating methods, such as evaporation.

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Claims

1. An electronic device comprising a substrate of III-V semiconductor material and an ohmic metal contact adhered to said substrate characterized in that:
   the ohmic contact comprises a thin film composed of at least tungsten and antimony.

2. The electronic device of claim 1 further characterized in that:
   the ohmic contact comprises substantially eighty to ninety-five per cent by weight of tungsten, five to ten percent by weight of antimony, and zero to fifteen percent by weight of indium.

3. The device of claim 2 further characterized in that:
   the substrate comprises crystalline indium phosphide.

4. A method of making an electronic device comprising the steps of applying a metal film to a substrate of III-V material so as to make an ohmic contact thereto characterized in that:
   tungsten and antimony are deposited by sputtering onto the substrate so as to form the metal film.

5. The method of claim 4 further characterized in that:
   the tungsten and antimony are sputtered simultaneously.

6. The method of claim 5 further characterized in that:
   tungsten, antimony and indium are sputtered simultaneously onto the substrate to make the metal film.

7. The method of claim 6 further characterized in that:
   the sputtering of tungsten and indium is done by dc sputtering and the sputtering of antimony is done by r-f sputtering.

8. The method of claim 7 further characterized in that:
   the substrate comprises crystalline indium phosphide.

9. The method of claim 8 further characterized in that:
   approximately eighty to ninety-five percent by weight of tungsten, approximately five to ten percent by weight of antimony and approximately zero to fifteen percent by weight of indium are deposited by sputtering to form the metal film.

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10. The method of claim 9 further characterized in that:

after sputtering, the substrate is annealed at an elevated temperature in excess of about 400°C.

Patentansprüche

1. Elektronische Einrichtung mit einem halbleitenden Substrat aus einem III-V-Material und einem ohmschen metallischen Kontakt auf dem Substrat,
dadurch gekennzeichnet,
daß der ohmsche Kontakt eine dünne Schicht aufweist, die mindestens Wolfram und Antimon enhält.

2. Einrichtung nach Anspruch 1,
dadurch gekennzeichnet,
daß der ohmsche Kontakt im wesentlichen 80 bis 95 Gew.% Wolfram, 5 bis 10 Gew.% Antimon und 0 bis 15 Gew.% Indium aufweist.

3. Einrichtung nach Anspruch 2,
dadurch gekennzeichnet,
daß das Substrat kristallines Indiumphosphit aufweist.

4. Verfahren zur Herstellung einer elektronischen Einrichtung, mit dem eine dünne metallische Schicht auf einem Substrat aus III-V-Material zur Bildung eines ohmschen Kontakts aufgebracht wird,
dadurch gekennzeichnet,
daß Wolfram und Antimon durch Kathodenzerstäubung auf dem Substrat zur Bildung der dünnen metallischen Schicht aufgebracht wird.

5. Verfahren nach Anspruch 4,
dadurch gekennzeichnet,
daß Wolfram und Antimon gleichzeitig durch Kathodenzerstäubung aufgebracht werden.

6. Verfahren nach Anspruch 5,
dadurch gekennzeichnet,
daß Wolfram, Antimon und Indium gleichzeitig durch Kathodenzerstäubung auf dem Substrat zur Bildung der dünnen metallischen Schicht aufgebracht werden.

7. Verfahren nach Anspruch 6,
dadurch gekennzeichnet,
daß Wolfram und Indium durch Gleichstrom-Kathodenzerstäubung und Antimon durch Hochfrequenz-Kathodenzerstäubung aufgebracht werden.

8. Verfahren nach Anspruch 7,
dadurch gekennzeichnet,
daß das Substrat kristallines Indiumphosphit aufweist.

9. Verfahren nach Anspruch 8,
dadurch gekennzeichnet,
daß etwa 80 bis 95 Gew.% Wolfram, 5 bis 10 Gew.% Antimon und 0 bis 15 Gew.% Indium zur Bildung der dünnen metallischen Schicht durch Kathodenzerstäubung niedergeschlagen werden.

10. Verfahren nach Anspruch 9,
dadurch gekennzeichnet,
daß das Substrat nach der Kathodenzerstäubung bei einer Temperatur oberhalb etwa 400°C getempert wird.

Revendications

1. Un dispositif électronique comprenant un substrat d'un matériau semiconducteur III-V et un contact métallique ohmique que l'on a fait adhérer au substrat, caractérisé en ce que :

le contact ohmique comprend une couche mince constituée au moins par du tungstène et de l'antimoine.

2. Le dispositif électronique de la revendication 1, caractérisé en outre en ce que :

le contact ohmique comprend approximativement 80 à 95% en masse de tungstène, 5 à 10% en masse d'antimoine et 0 à 15% en masse d'indium.

3. Le dispositif de la revendication 2, caractérisé en outre en ce que :

le substrat consiste en phosphure d'indium cristallin.

4. Un procédé de fabrication d'un dispositif électronique comprenant les étapes qui consistent à appliquer une couche de métal sur un substrat en matériau III-V, de façon à former un contact ohmique avec le substrat, caractérisé en ce que :

on dépose du tungstène et de l'antimoine par pulvérisation cathodique sur le substrat, de façon à former la couche de métal.

5. Le procédé de la revendication 4, caractérisé en outre en ce que :

on effectue simultanément la pulvérisation cathodique de tungstène et d'antimoine.

6. Le procédé selon la revendication 5, caractérisé en outre en ce que :

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on effectue simultanément la pulvérisation cathodique de tungstène, d'antimoine et d'indium sur le substrat pour former la couche de métal.

7. Le procédé de la revendication 6, caractérisé en outre en ce que :

on effectue la pulvérisation cathodique de tungstène et d'indium en procédant par pulvérisation cathodique à courant continu, et on effectue la pulvérisation cathodique d'antimoine en procédant par pulvérisation cathodique radiofréquence.

8. Le procédé de la revendication 7, caractérisé en outre en ce que :

le substrat consiste en phosphure d'indium cristallin.

9. Le procédé de la revendication 8, caractérisé en outre en ce que :

on dépose par pulvérisation cathodique, pour former la couche de métal, environ 80 à 95% en masse de tungstène, environ 5 à 10% en masse d'antimoine et environ 0 à 15% en masse d'indium.

10. Le procédé de la revendication 9, caractérisé en outre en ce que :

après pulvérisation cathodique, on recuit le substrat à une température élevée dépassant environ 400°C.