

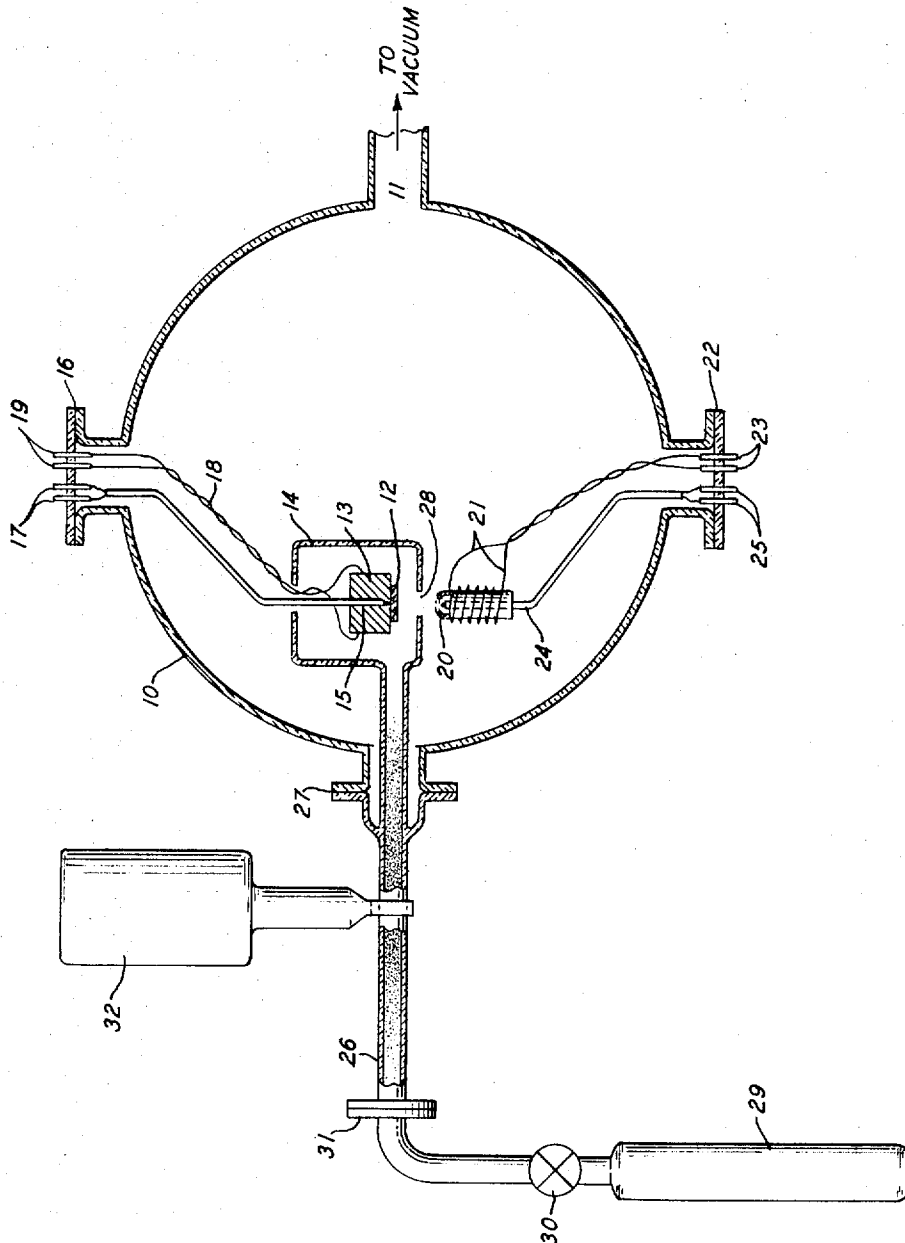
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D. KAHNG ET AL

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VACUUM EVAPORATION DEPOSITION OF GROUP III-A METAL NITRIDES

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INVENTORS D. KAHNG
BY B.B. KOSICKI

[Signature]

ATTORNEY

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VACUUM EVAPORATION DEPOSITION OF
GROUP III-A METAL NITRIDES

Dawon Kahng, Somerville, and Bernard B. Kosicki, New Providence, N.J., assignors to Bell Telephone Laboratories, Incorporated, Murray Hill and Berkeley Heights, N.J., a corporation of New York

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11 Claims

ABSTRACT OF THE DISCLOSURE

The specification describes a process for depositing nitride films of the group III-A metals. The process relies on a modified two-source evaporation technique in which the nitrogen becomes activated by passing through a plasma prior to reaction at the substrate surface. In this way highly reactive gas species can be produced without plasma bombardment of the substrate. Epitaxial deposits are also described.

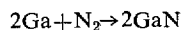
This invention relates to a process for depositing insulating and semiconducting films of the nitrides of the group III-A metals.

The deposition of nitride films of gallium and, to a lesser but significant extent of aluminum and indium, presents an especially difficult problem. It is desirable from the standpoint of purity to restrict the reactants in the deposition mechanism to the constituent elements. Once this restriction is imposed, possible commonly used techniques for film growth are limited to evaporation and cathode sputtering. The thermal reaction between Ga and N₂ is often slow, if possible at all, due to the large dissociation energy for N₂.

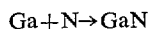
Evaporation is an unlikely approach because of the very large difference in vapor pressures of the constituent elements. Two-source evaporation is unattractive due to the large dissociation energy for N₂ molecules.

In the case of gallium nitride, sputtering, using a two-source technique, involves a liquid Ga source, with the attendant difficulties of making electrical contact while maintaining source purity. Sputtering also produces ion bombardment of the substrate, a condition often tolerated but recognized as undesirable.

This invention is directed to a modification of a two-source evaporation technique. In this process the substrate and the surrounding surfaces are not exposed to high energy ions or electrons as in sputtering or plasma deposition processes. This results in a film having a more ordered, defect-free structure and eliminates the chance of accidental sputtering from surrounding surfaces onto the substrate. As mentioned above the large dissociation energy of nitrogen severely limits its reactivity toward gallium according to the normal reaction



According to the invention, this difficulty is overcome by providing the dissociation energy from a high energy discharge located apart from the reaction region. Atomic nitrogen produced by the discharge flows into the reaction region where it reacts according to the more favorable reaction.



Films of these materials have useful semiconducting properties, some of which may not as yet be realized. One immediate use of the films is for passivation of III-V compounds, such as gallium arsenide and gallium phosphide. These compounds are difficult to passivate by conventional techniques because of surface degradation

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through dissociation and volatilization of the constituent elements at the high temperatures normally used for depositing insulating films. Films deposited on these compounds according to this invention can protect against this degradation while a second passivating film is being applied by conventional means. In some cases the nitride film itself may be sufficient for passivation.

These and other aspects of the invention will be more fully appreciated from a consideration of the following more detailed description. In the drawing:

The figure is a schematic representation of an apparatus suitable for the practice of this invention.

In the figure a cylindrical vacuum chamber 10 is shown with an opening 11 connected to a molecular sieve pump (not shown) for establishing and maintaining a vacuum in the chamber 10. Within the chamber the substrate 12 is mounted on pedestal 13 which in turn is held inside a quartz reaction chamber 14. The pedestal 13 is equipped with a thermocouple 15 terminating at the outside of vacuum seal 16 with connections 17, and electrical wires 18 and associated connections 19 for independently heating the substrate 12. The Group III-A metal is contained in an elongated quartz crucible 20, provided with heating coil 21. The coil is connected through vacuum seal 22 to terminals 23. The source also is equipped with a thermocouple 24 connected to terminals 25. The reaction chamber 14 is integral with tube 26 and both are sealed to the chamber 10 at the vacuum seal 27. An opening 28 in the reaction chamber allows access for the Group III-A metal. A nitrogen source 29 is connected through valve 30 and vacuum seal 31 to the quartz tube 26. A microwave source 32 is arranged to establish a discharge over the hatched region of the tube 26. This provides the dissociation energy for the nitrogen and supplies a continuous flow of atomic or active nitrogen to the reaction chamber 14.

The following embodiment is given as exemplary of the process of the invention. It describes the deposition of a gallium nitride film. The chamber 10 was pumped down to approximately 10⁻¹⁰ torr to remove residual gaseous impurities. Very pure nitrogen (<1 molar p.p.m. impurities) was admitted by opening valve 30. The discharge was established using a 300 watt microwave generator at 2450 mc. Nitrogen was flowed through tube 26 at a relatively high rate to purge the impurities generated by the interaction of the discharge with the tube walls. The flow rate of nitrogen was then adjusted to give a pressure of about 50×10⁻³ torr. The gallium contained in the source crucible 20 was heated to approximately 850° C. The substrate temperature was approximately 600° C. Deposition of pure gallium nitride occurred at a rate of approximately 1 μm./hr. Films deposited on amorphous silica and gallium arsenide substrates were compared to determine the epitaxial capability of the process. On fused silica the crystal orientation of the C-axis of the deposited films was parallel or perpendicular to the growth plane and evidenced little control. On (111) oriented gallium arsenide substrate the C-axis of the film was normal to the growth plane and evidenced strong orientation. For non-epitaxial films the material of the substrate is largely unimportant. In these cases it is not essential to beat the substrate. For epitaxial growth the lattice mismatch should preferably be below 30 percent and the substrate should be heated to above 450° C. to encourage epitaxial orientation. In the case of gallium nitride films, lattice match is acceptable for substrates of gallium arsenide, gallium phosphide and gallium arsenide-gallium phosphide mixtures, as well as oriented sapphire and ZnO.

An essential feature of the process of the invention is the provision of highly reactive atomic nitrogen to the

reaction region. It is distinguished in that the source of the dissociation energy is separate from the immediate reaction environment. This means that the visible portion of the plasma used for producing atomic nitrogen in this example should be maintained separate from the substrate, a spacing of a few centimeters being adequate to ensure that ion or electron bombardment of the substrate and surrounding surfaces is avoided.

In the apparatus described above the nitrogen pressure can be varied over the range of 0.001 torr to 0.1 torr. Below 0.001 torr the pressure of atomic nitrogen is so low that a practical growth rate is difficult to achieve. About 0.1 torr the vapor pressure of gallium required is inconveniently high. It is more meaningful perhaps to prescribe the quantities of the reactants in the region of the substrate. This takes into account several independent variables such as the efficiency of the high energy discharge, the nitrogen gas pressure and flow rate, the temperature of the gallium source, the spacing between the source and substrate, etc. If the absolute partial pressure of atomic nitrogen in the deposition region drops below 10^{-7} torr a useful growth rate will be difficult to obtain. The ratio of the pressure of atomic nitrogen to the pressure of gallium vapor should be greater than 10. This restriction is imposed by the fact that gallium atoms stick to the substrate while nitrogen atoms conveniently do not. Hence, excess atomic nitrogen ensures a more stoichiometric film. The preferred operating pressures are at least 10^{-3} to 10^{-6} torr for atomic nitrogen and 10^{-4} to 10^{-7} torr for gallium.

It is significant to point out that the reactivity of the Group III-A elements to molecular nitrogen is low enough so that the sources do not nitride excessively. Other sources may react to the point where continuous evaporation is difficult or impossible. Whereas this description is largely concerned with depositing gallium nitride, aluminum nitride, indium nitride and thallium nitride behave in the same way and can be deposited under essentially the same conditions. Gallium nitride-aluminum nitride mixtures and mixed films including indium and thallium can be conveniently produced by this technique either by introducing a second source (crucible, or by using a mixed source. The energy gap as well as other properties of the film can be tailored to a specific need by varying the relative proportions of the constituent metals. In this connection the generic reference to Group III-A metals herein should be construed as including mixtures of those metals. Dopants such as Group II or Group VI elements can also be introduced in these films by providing a separate source for these materials, or mixing the impurity in the metal or nitrogen source.

Non-stoichiometric films can be grown by this technique by varying the parameters which determine the relative amounts of reactants present in the reaction region. While this flexibility may in some cases be advantageous there are situations in which a film rich in the Group III element is undesirable, for instance, where the objective is an insulating film. In such cases precise control over the stoichiometry during deposition is not vital since a film rich in the Group III metal can be exposed to a post-deposition anneal to provide a more nearly ideal stoichiometry. For instance, films deposited by the above technique were found, in some instances, to exhibit a yellowish color attributable to excess gallium. These films were treated in nitrogen at 1000 atmospheres

and 700° C. until the film became clear, evidencing elimination of excess gallium.

The discharge described herein is a microwave discharge created and maintained by a cavity external of the reaction vessel. This arrangement has the advantage of voiding possible contamination from the presence of electrodes in the reaction environment. However, other types of high energy discharges, such as a D.C. discharge, can also be used. Any such electrical discharge capable of producing an intense visible glow will be effective to some extent for the purpose of the invention.

Various additional modifications and extensions of this invention will become apparent to those skilled in the art. All such variations and deviations which basically rely on the teachings through which this invention has advanced the art are properly considered within the spirit and scope of the invention.

What is claimed is:

1. A process for depositing a nitride of a group III-A metal on a substrate comprising the steps of mounting the substrate adjacent to a source of the group III-A metal in a vacuum chamber, flowing nitrogen gas through a high energy discharge spaced from the substrate whereby atomic nitrogen is formed and subsequently confining said atomic nitrogen with the substrate in a restrictive space and simultaneous heating the group III-A metal source outside of said restricted space to evaporate the group III-A metal, so that atomic nitrogen and the group III-A metal vapor meet and react at the substrate surface to produce the group III-A nitride.
2. The process of claim 1 wherein the atomic nitrogen and the group III-A metal are present at the substrate surface in amounts of at least 10^{-4} to 10^{-6} torr and 10^{-5} to 10^{-7} torr respectively.
3. The process of claim 1 wherein the substrate is heated to produce an epitaxial deposit.
4. The process of claim 1 wherein the group III-A metal is gallium.
5. The process of claim 4 wherein the gallium source temperature is at least 750° C. and the pressure in the vacuum chamber is in the range of 0.001 torr to 0.1 torr.
6. The process of claim 4 wherein the substrate is selected from the group consisting of gallium arsenide, gallium phosphide and mixtures thereof, aluminum oxide and zinc oxide.
7. The process of claim 6 wherein the substrate is heated to a temperature of at least 450° C. to obtain an epitaxial deposit.
8. The process of claim 1 wherein the group III-A metal is aluminum.
9. The process of claim 1 wherein the group III-A source is a mixture of aluminum and gallium.
10. The process of claim 1 wherein the source includes a source of impurities for controlling the conductivity type and level of the deposited film.
11. A coated substrate prepared by the process of claim 1.

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ROBERT K. MIHALEK, Primary Examiner

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