

PATENT SPECIFICATION

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(72) Inventors JON CHARLES GOLDMAN
JAMES BRIAN PRICE and
LARRY DONALD MCMILLAN



(54) METHOD FOR THE LOW PRESSURE PYROLYTIC DEPOSITION OF SILICON NITRIDE

(71) We, MOTOROLA, INC., a corporation organised and existing under the laws of the State of Delaware, United States of America, of 1303 East Algonquin Road, Schaumburg, Illinois 60196, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the low pressure pyrolytic deposition of silicon nitride onto a heated substrate and to substrates having uniform films of silicon nitride deposited thereon. More particularly, this invention relates to the deposition of silicon nitride by reacting a halosilane with ammonia in a vacuum or near vacuum. The term "halosilane" includes only compounds including silicon, hydrogen and a halide.

Silicon nitride (Si_3N_4) is a dense, chemically inert, dielectric material of extreme hardness, low thermal conductivity and high resistance to molecular diffusion. These properties have made silicon nitride an attractive and valuable material for a wide range of applications. For example, it is useful in the fabrication of semiconductor devices, as oxidation masks, capacitor dielectrics for bit storage, masking layers, polish retarders, etc.

Various methods for depositing silicon nitride are known, but while the processes described in the prior art are functional in certain applications, they present drawbacks in other areas.

It is an object of the invention to provide an improved method for the pyrolytic deposition of silicon nitride.

It is a further object of this invention to provide an economical process for the deposition of silicon nitride characterized by high throughput.

It is another object of this invention to

provide uniform and continuous coatings of silicon nitride which are free from defects.

It is still another object of this invention to provide improved yields of semiconductor devices made from silicon wafers having silicon nitride deposited thereon.

In accordance with this invention, there is provided a method for the low pressure pyrolytic deposition of silicon nitride upon a heated substrate which comprises contacting a mixture of a halosilane as hereinbefore defined and ammonia with said substrate in a vacuum or near vacuum in a resistance-heated furnace.

The invention will now be described by way of example only with particular reference to the accompanying drawings wherein:

Figure 1 shows a schematic view of an apparatus for use in the process of this invention, and

Figure 2 shows an isometric view, partly broken away, of a furnace tube loaded with wafers and suitable for use in the practice of this invention.

A furnace tube 10 is heated by resistance heat coils 12 adjusted to give the desired temperature as described in detail below.

A gas panel generally referred to as 14 leads to the inlet end of furnace tube 10. This gas panel contains a source of halosilane 16, nitrogen 18 and ammonia 20, which are admitted to the furnace tube by opening valves 22, 24, 26 and 28. The halosilane is any monohalogenated or polyhalogenated silane, including the chlorosilanes, fluorosilanes, bromosilanes, and iodasilanes. Preferably chlorosilanes, such as chlorosilane, dichlorosilane, and trichlorosilane are employed. The flow of gases are controlled by flow meter valves 30, 32 and 34. An end cap 36 is in engagement with furnace tube 10 to provide a vacuum seal within the tube, and the pressure is read by vacuum gauge 38. Exhaust 40 serves to vent by-products

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and unreacted, starting materials from the tube. As shown, the furnace tube holds a quartz boat 42 loaded with a plurality of silicon wafers 44, which are positioned with their broad surfaces perpendicular to the cylindrical axis of the tube. The wafer positioning is clearer in Fig. 2. Preferably, a spacing of 50 to 500 mils between wafer surfaces is employed, with as many wafers as can be accommodated by the tube being processed at one time. While the type of wafer positioning shown in the drawings provides for maximum utilization of the tube, other means of positioning the wafers are contemplated. Furthermore, the process can be carried out in different types of vacuum apparatus.

In carrying out the process of this invention, the furnace tube is heated to the appropriate temperature for the particular halosilane and purged with nitrogen. Then the boat containing silicon wafers is loaded into the tube. The selected temperature should be high enough to give an acceptable growth rate while minimizing the competitive thermal decomposition of the halosilane to produce silicon. Generally a temperature between 650°C and 1000°C is employed.

Another feature of this invention is that a temperature ramp can be established within the furnace tube. Thus, there can be a temperature variation along the tube, up to 100°C, and preferably from 10°C to 50°C, with the lowest temperature being near the gas inlet end of the tube and the highest temperature near the opposite end of the tube. It has been found that utilizing a temperature ramp allows more flexibility in optimizing down-the-boat uniformity and deposition rate. Higher temperatures increase both the deposition rate and the source gas depletion. Source gas depletion decreases wafer uniformity down the boat. Since higher deposition rates are desirable to increase throughput, one compensates for source gas depletion by temperature ramping, with the more depleted end at the highest temperature.

After the boat has been loaded into the tube and the desired temperature achieved, a vacuum less than 50 μ is established. Then, ammonia and halosilane are admitted to the tube, bringing the pressure to from 300 millitorr to 10 torr. The flow is regulated so that the mole ratio of ammonia to halosilane is from 1 to 500:1. Furthermore, the ammonia is metered into the furnace tube at a rate between .01 and 10 cc/sec, while the halosilane is metered into the tube at a rate between .01 and .5 cc/sec. It has been found that the growth of silicon nitride under these conditions is about 5 to 100 Å/minute; the process is continued until the desired thickness is deposited on

the wafers. For most semiconductor applications, a thickness of 200—2000 Angstrom of layers is desired, but the process of the invention is suitable to deposit layers of any thickness.

The silicon nitride layers produced according to this process have been found to have many advantages over those produced by prior art processes. Thus, the peripheral ring of thicker nitride found on wafers treated with silane and ammonia under vacuum is eliminated. Furthermore, silicon or silicon nitride dust formation and boat marks found in the aforementioned silane process were reduced to an insignificant level. Since the silicon nitride layers are uniform, more devices can be made from semiconductor wafers treated in accordance with this invention, further enhancing the attractiveness of the process.

The following example will serve to illustrate the practice of this invention.

One hundred fifteen precleaned 3-inch diameter silicon wafers were loaded into a three-rail quartz boat 16 inches long with 3/32 inch wafer spacing; in accordance with standard diffusion techniques, five dummy wafers were placed at each end of the boat. Then the boat was placed in a 101 mm outside diameter quartz tube in a thermo furnace. The temperature profile of the furnace was ramped so that the thermocouple measurements at three equidistant points covering the center 20 inches of the furnace gave readings of 730°C, 750°C and 770°C respectively, with the lowest temperature at the end adjacent to the gas inlet. The furnace was evacuated to less than 50 μ and purged with nitrogen for ten minutes at a pressure of 2 torr. Then the nitrogen was turned off and the system pumped down to a pressure less than 50 μ . Ammonia was injected at a flow rate of .24 cc/sec for one minute. Then dichlorosilane was injected at a flow rate of .02 cc/sec while continuing the injection of ammonia. After 60 minutes, the dichlorosilane flow was terminated and the ammonia flow was terminated one minute later. These flow rates correspond to a molar ratio of ammonia to dichlorosilane of about 12 to 1. Then the furnace was pumped to a pressure of less than 50 μ and purged with nitrogen for five minutes at a pressure of 2 torr. The vacuum valve was closed and the system back-filled with nitrogen. The boat was unloaded and the wafers evaluated. They were found to have a 1000Å thick layer of silicon nitride which was uniform from wafer to wafer $\pm 10\%$, and around the wafer $\pm 1\%$, the wafers exhibited no haziness and no boat marks.

WHAT WE CLAIM IS:—

1. A method for the low pressure

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- pyrolytic deposition of silicon nitride upon a heated substrate which comprises contacting a mixture of a halosilane (as hereinbefore defined) and ammonia with said substrate in a vacuum or near vacuum in a resistance-heated furnace.
2. A method as claimed in claim 1 wherein a temperature of from 650°C to 1000°C is employed.
3. A method as claimed in claim 2 wherein said halosilane is a chlorosilane.
4. A method as claimed in claim 3 wherein a vacuum of 300 millitorr to 10 torr is employed.
5. A method as claimed in claim 3 wherein said chlorosilane is dichlorosilane.
6. A method as claimed in claim 5 wherein a vacuum of 300 millitorr to 10 torr is employed.
7. A method as claimed in claim 1 wherein the temperature variation along the length of the resistance furnace is up to 100°C with the lowest temperature being near the gas inlet end of the furnace.
8. A method as claimed in any preceding claim for depositing a silicon nitride film of uniform thickness on a semiconductor substrate, said film being provided by reacting a halosilane with ammonia in a vacuum in a resistance-heated furnace.
9. Silicon nitride when pyrolytically deposited by the method claimed in any preceding claim.

For the Applicants:
F. J. CLEVELAND & COMPANY,
Chartered Patent Agents,
40—43 Chancery Lane,
London WC2A 1JQ.

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