

In conclusion, a new SOI structure has been proposed and fabricated by utilizing Si-MBE growth on porous silicon, silicon island patterning, and the subsequent lateral enhanced oxidation of the porous silicon. A RHEED pattern of Si-MBE film grown on porous silicon without preheating shows a clear  $7 \times 7$  superlattice pattern which is characteristic of a high-quality Si(111) crystal structure. After patterning, Si-MBE film,  $7.0 \mu\text{m}$  wide and  $0.35 \mu\text{m}$  thick, is completely isolated by  $\text{SiO}_2$  formed from the Si-MBE film.

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## A new technique for getting oxygen and moisture from gases used in semiconductor processing

J. R. Shealy<sup>a)</sup> and J. M. Woodall<sup>b)</sup>

*School of Electrical Engineering, Cornell University, Ithaca, New York 14853*

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A technique for the removal of small amounts of water vapor and oxygen from hydrogen and nitrogen is described in which the gas is purified by bubbling it through a gallium-indium-aluminum melt at room temperature. Using this technique, dew points of  $\leq -80^\circ\text{C}$  are achieved when the starting gas contains as much as one part per thousand of water vapor.

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The purity of gases used in semiconductor processing is of prime importance in the majority of device fabrication schemes. Metallurgy on semiconductors involving materials which are highly reactive with oxygen such as aluminum and titanium<sup>1</sup> requires ambients with very low levels of oxygen and water vapor to prevent oxidation. Standard techniques for the purification (removal of oxygen and water vapor) of process gases include (i) the catalytic conversion of oxygen to water vapor and subsequent removal of the water vapor using a molecular sieve, (ii) the use of a gettering furnace usually containing titanium for the removal of both oxygen and water vapor from most inert gases, and (iii) the use of a hot palladium diffusion cell for the removal of impurities from hydrogen. With the first method, the use of corrosive gases and the extent of contamination from sieve materials such as alumina silicates or activated charcoal is questionable. This second method using the titanium gettering furnace is not applicable for the purification of nitrogen and corrosive gases and its capacity for the removal of oxygen or water vapor is somewhat limited. Finally, the hot palladium diffusion cell is applicable to hydrogen only and is susceptible to damage (microcracks in the palladium) if allowed to cool with hydrogen present.

This letter describes the purification of process gases using free aluminum as the primary gettering element in a gallium indium solution at room temperature. The method

to be described is simple to integrate in existing semiconductor processing equipment and has the following advantages over the methods mentioned above:

(i) The availability of very high purity gallium, indium, and aluminum eliminates concern for possible contamination of the process gas from trace impurities in these group III transition metals. The vapor pressure of these metals at room temperature is sufficiently low to avoid their incorporation in to the process gas being treated.

(ii) By preparing a two-phase solution consisting of the liquid ternary saturated with aluminum and solid aluminum the solution can remain saturated with aluminum as the aluminum is consumed by oxidizing in the presence of the process gas. This allows a very high capacity for the removal of oxygen and water vapor.

(iii) Because this method of purification is done at room temperature many gases may be treated which would thermally decompose at the moderate temperature used in gettering furnace techniques. Also, a variety of corrosive gases would be applicable providing they do not sufficiently react with Ga, In, and aluminum at room temperature.

The apparatus used for all experiments is shown in Fig. 1. The incoming process gas was either hydrogen or nitrogen. The hydrogen was prepared by diffusion through a palladium cell at  $300^\circ\text{C}$ . The nitrogen was taken from the "boil off" of a liquid nitrogen source. The flow used in the experiment was fixed at approximately one standard liter per minute.

After passing through a flow meter, the gas was bubbled

<sup>a)</sup> General Electric Company, Discrete Semiconductor Device Center, Syracuse, NY 13221.

<sup>b)</sup> IBM Thomas J. Watson Research Center, Yorktown Heights, NY 10598.

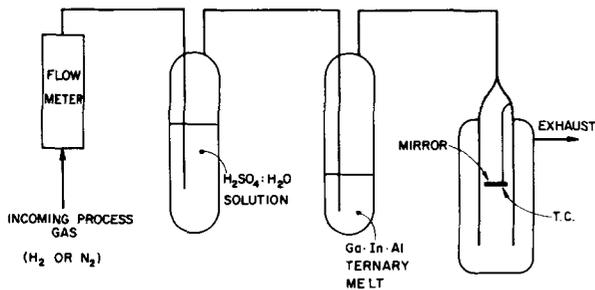


FIG. 1. Schematic diagram of apparatus used to getter  $O_2$  and moisture.

through an aqueous sulfuric acid solution in order to generate a known partial pressure of water vapor in the incoming gas. This solution contained 78% by volume of sulfuric acid. A total of 5 g of dionized water was present in this solution.

Following the introduction of the water vapor, the gas was bubbled through a ternary melt of gallium, indium, and aluminum. The melt was prepared by first dissolving 10 g of indium into 100 g of gallium at  $40^\circ C$ . This produced a liquid solution at room temperature ( $\sim 24^\circ C$ ).<sup>2</sup> Excess aluminum was then added to the gallium indium solution until saturation of aluminum was achieved at room temperature. Approximately 1.8 g of aluminum was dissolved into the liquid melt. The melt was placed in a quartz bubbler which resulted in an equivalent pressure head of 5-mm Hg.

After bubbling through the ternary melt, the gas was passed through a flask designed to measure the dewpoint of moisture in the gas. This flask contains a mirror as shown in Fig. 1 which deflected the incoming gas flow around it. An iron-constantine thermal couple was used to monitor the mirror temperature. The flask was slowly cooled by emerging the flask in liquid nitrogen. The dewpoint was determined by observing the change in the reflectivity of the mirror due to ice condensation from the moisture in the incoming gas. The experimental error for this dewpoint experiment is estimated to be  $\pm 5^\circ C$ .

Prior to the use of the aqueous sulfuric acid solution and the gallium-indium-aluminum melt, the dewpoint of the background gas was determined. In addition, the dewpoint of the gas passing through the aqueous sulfuric acid solution was measured with and without the gallium-indium-aluminum melt.

The use of aluminum as an oxygen gettering element has the primary advantage that its oxide ( $Al_2O_3$ ) is stable and has a low vapor pressure. It has been shown that small amounts of aluminum added to a gallium effusion cell in molecular beam epitaxy has substantially reduced the introduction of gallium oxide into the growth flux.<sup>3</sup> However, the use of solid metallic aluminum is not effective for oxygen gettering because its thin protective native oxide prevents further oxidation. The use of the gallium-indium-aluminum ternary melt provides a convenient means for continuously reacting aluminum with oxygen and moisture at room temperature. As the oxygen gettering proceeds the aluminum oxide floats to the top of the melt.

The dewpoint of the starting gases was determined to be approximately  $-80^\circ C$  which corresponds to less than 1 ppm of moisture. Measurements of dewpoints below

TABLE I. Dewpoint data taken for times after the process gas was treated by the gallium-indium-aluminum melt at room temperature.

Dewpoint ( $^\circ C$ )	Time (h)
$-80$	0
$-80$	1
$-80$	10
$-70$	25
$-60$	40
$-45$	70

$-80^\circ C$  were not attempted because the time required for condensation on the mirror was in excess of several hours. Upon the addition of the aqueous sulfuric acid solution, the gas bubbled through this solution had a dewpoint of  $-20^\circ C$ . This corresponds to 1000 ppm of moisture in the gas which is in fair agreement with vapor pressure data in the literature.<sup>4</sup> Passing the gas with 1000 ppm of moisture through a *gallium-indium solution had little or no affect on the gases' dewpoint!* With the addition of aluminum to the melt, the dewpoint of the gas was initially reduced to below  $-80^\circ C$ . Table I summarizes dewpoint data taken for times after the gas was introduced through the ternary melt.

As indicated by the table, the melt is slowly becoming saturated with water vapor after approximately 25 h. This is due to the consumption of free aluminum in the melt by oxidation. Small amounts of aluminum oxide on the surfaces of the melt were observed after 1 h and its presence was more pronounced as the experiment proceeded. It appears that approximately 1 g of aluminum in solution with gallium and indium will purify approximately 1500 l of process gas containing 1000 ppm of water vapor.

Also, we have performed preliminary experiments with two reactive gases:  $AsH_3$  and  $Ga(CH_3)_3$  commonly used for the chemical vapor deposition of GaAs. We have found that both  $AsH_3$  and  $Ga(CH_3)_3$  bubbling through the Al-Ga-In melt at room temperature do not decompose; and, thus, it is expected that the melt will getter  $O_2$  and  $H_2O$  from these reactive gases as well as it does from  $H_2$  and  $N_2$ .

In conclusion, a relatively simple means for removing oxygen and water vapor from hydrogen and nitrogen was described. Other gases used in processes like chemical vapor deposition (CVD) are likely to be applicable. This would be important since the presence of small amounts of oxygen (as little as 1 ppm) has been shown to be the primary cause for heavy compensation of AlGaAs grown by metal organic CVD.<sup>5</sup> It should be possible to treat the incoming gases in this process, namely arsine and metal organic vapors diluted in hydrogen, with the gallium-indium-aluminum ternary melt at room temperature resulting in an improvement in the quality of AlGaAs. The application of this technique to metal organic CVD is currently under investigation.

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## Organic-on-inorganic semiconductor contact barrier devices

S. R. Forrest, M. L. Kaplan, P. H. Schmidt, W. L. Feldmann, and E. Yanowski  
Bell Laboratories, Murray Hill, New Jersey 07974

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The organic compound 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) has previously been observed to undergo a large increase in conductivity on irradiation with energetic particle beams. In this letter, we describe the electrical characteristics of novel rectifying junctions employing unirradiated PTCDA vapor deposited onto 10- $\Omega$  cm *p*-Si substrates. The PTCDA-Si contact barrier has a height of  $\phi_B = 0.74$  eV. The resulting diodes undergo avalanche breakdown at  $V_B = 230$  V, and exhibit current densities at  $\frac{1}{2} V_B$  of  $\leq 50 \mu\text{A}/\text{cm}^2$ . In addition, the forward current-voltage ( $I_F - V$ ) characteristics are strongly dependent on the contact metal used on the top PTCDA surface. The best results obtained were for diodes employing Ti contacts which gave nonhysteretic, stable  $I_F - V$  characteristics with an ideality factor of  $n = 1.7$ . Several properties of the as-deposited PTCDA are also discussed. The rectifying characteristics reported here, coupled with the properties of irradiated PTCDA, suggest many unique device applications.

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Devices that utilize the electronic properties of nonpolymeric organic compounds have been the subject of investigation for more than two decades.<sup>1</sup> In particular, solar cells using metal/organic/metal sandwiches,<sup>2,3</sup> diodes employing charge transfer complexes,<sup>4</sup> and memory devices<sup>5</sup> have been the focal point of recent work. The organic compound<sup>6</sup> 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) has recently<sup>7</sup> been observed to undergo a large increase in conductivity on irradiation with energetic particle beams. In this letter we describe novel devices where unirradiated PTCDA is vacuum sublimed onto *p*-type Si substrates forming a rectifying junction. We believe that this is the first report of diodes fabricated using nonpolymeric organic thin films deposited on inorganic semiconductor substrates. This is in contrast to devices prepared using monolayer organic insulators deposited by Langmuir-Blodgett techniques on InP.<sup>8</sup> The devices have current-voltage ( $I - V$ ) characteristics similar to those of abrupt junction Si diodes and exhibit high breakdown voltages and low reverse-current densities dominated in some cases by generation and recombination within the Si bulk. The forward characteristics depend strongly on the contact metal used. The PTCDA-on-inorganic semiconductor contact barrier diodes are easy to fabricate and have good electrical properties. In addition, metal-PTCDA-metal sandwiches are described which were used to determine several properties of the as-deposited PTCDA films.

In Fig. 1(a) we show the structural formula of a molecule of PTCDA. The aromatic dianhydride is deposited from the vapor resulting in polycrystalline, transparent red, thin films. The degree of crystallinity depends on deposition conditions as discussed below. Figure 1(b) is a schematic

cross section of the PTCDA on *p*-Si diodes. To fabricate the diodes, prior to deposition the polycrystalline PTCDA<sup>7</sup> is purified by gradient sublimation in a Pyrex tube heated between 400 and 100 °C in a vacuum of  $\sim 10^{-2}$  Torr. This allows for separation of the more volatile impurities in the source material. Ohmic back contact to the (100), boron-doped, 10- $\Omega$  cm *p*-Si wafer is obtained by evaporation and sintering of Al. The top Si surface is cleaned in HF, water, and ethyl alcohol to remove residual dirt and oxide layers. The PTCDA is then sublimed onto the top Si surface at thicknesses between 1000 and 2000 Å in a vacuum of  $10^{-6}$

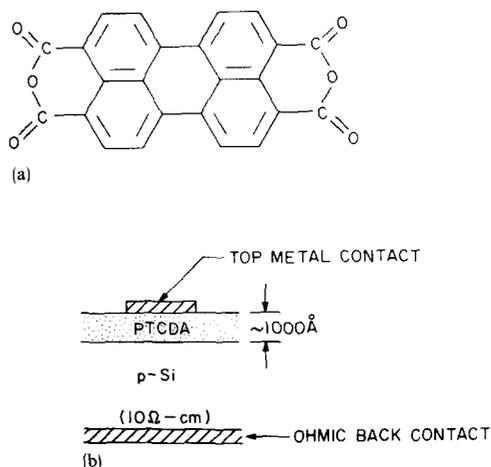


FIG. 1. (a) Molecular structural formula of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA). (b) Schematic cross section of metal/PTCDA/*p*-Si device. Area of top contact =  $2.5 \times 10^{-4} \text{cm}^2$ .