III-V Semiconductor Vapour Growth

APPLICATION OF PALLADIUM-SILVER DIFFUSION MEMBRANES AND THE RESTORATION OF HYDROGEN OUTPUT

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The class of semiconductors based on Group III and V elements can be fabricated into efficient light emitters and lasers for the red and near infrared spectral regions. Commercially these devices are used as optical read-write systems, such as those found in compact disc players and data storage systems. An important III-V alloy commonly used in semiconductor lasers is $Al_{(x)}Ga_{(1-x)}As$, where $x = 0$ to 0.35. The aluminium component of the alloy is particularly sensitive to oxygen, which is readily incorporated during vapour phase epitaxial growth. Substitutional oxygen within the crystal lattice lowers the optical efficiency of the material by creating centres which trap minority carriers, the precursors to light emission.

In order to realise large scale uniform single crystal layers of AlGaAs the epitaxial growth technique most favoured is Metal Organic Vapour Phase Epitaxy (MOVPE). The precursors for this process are usually trimethylaluminium, trimethylgallium and arsine, which are transported to a heated (700°C) GaAs substrate by a carrier gas of ultra pure hydrogen. Oxygen, inadvertently incorporated during crystal growth, can arise from a number of sources including the hydrogen carrier, the arsine, alkoxide impurities in the metal-alkyl and leaks, either real or virtual, within the stainless steel pipework of the reactor.

High purity hydrogen can be generated by a number of techniques including boil off from the liquid, gettering using a metalorganic polymer or diffusion through a series of palladium-silver membranes (1). The latter is potentially the most efficient as the unit can be made leak tight to all gases except hydrogen.

The diffusion of hydrogen through 23 per cent palladium-silver membranes is a well established technique for purifying commercial grade cylinder hydrogen (2). The hydrogen diffusion process results in the dissociation of each molecule into two protons and two electrons, followed by diffusion through the palladium-silver lattice. On reaching the high purity region the protons and electrons combine to reform hydrogen. With appropriate equipment hydrogen of 99.9999 per cent purity or better may be obtained, suitable for use as a transport medium for metal alkyl vapour and as a carrier gas during the manufacture of semiconductor materials (3). Generally the membrane takes the form of a 1.5 mm internal diameter tube sealed at one end and internally supported. Hydrogen is diffused from the outer to the inner surface of the tube using an input pressure of 280 psi. A number of these membranes are brazed into a stainless steel output manifold.

Within this department, hydrogen is obtained from an "EP–20" diffusion unit, which has an output of 20 standard litres per minute at an operating temperature of about 300°C and an input pressure of 280 psi. The purity of the hydrogen output is better than can be determined by simple analytical measurements, necessitating mass spectrography for accurate analysis. Indeed the luminescence efficiency of unintentionally doped AlGaAs from a number of reactors indicates that the purity of the hydrogen exiting from the palladium-silver membranes is not a controlling factor of the overall material quality.

Should the hydrogen supply to the diffusion unit become depressurised, it can be arranged for the input to be automatically switched to nitrogen. The exchange of nitrogen for hydrogen promotes reverse diffusion through the membrane and the removal of hydrogen from the diffuser and associated equipment. In addition, cooling the membrane in the absence of hydrogen prevents embrittlement of the fragile diffusion tubes.

On a number of occasions, when cylinder hydrogen has been re-introduced to the diffuser after a nitrogen purging process, there has been a serious reduction in the rate of hydrogen output, apparently due to some form of contamination of the membrane. The nitrogen purge was undertaken while the unit was at 310°C using high purity gas, but without an oxygen removal catalyst in the input line. The low hydrogen output could therefore result from the formation of an oxide on the surface of the membrane. One such faulty membrane was removed from its housing and etched for 2 minutes in a hydrofluoric acid solution made from 40 per cent hydrofluoric acid stock diluted by 50. A simple PVC tube, closed at one end, served as a container for the etchant. The palladium-silver membrane tube was then washed for several minutes in a flow of de-ionised water and dried at 100°C for about 15 minutes. The hydrofluoric acid treatment was choosen to promote the formation of silver fluoride, which as the hydrate has a high water solubility. The reassembled diffuser initially gave only a modest improvement in hydrogen flow but on increasing the temperature from 310 to 360°C the full output of the unit was realised. The operating temperature was then returned to 310°C without any reduction in the pure hydrogen gas output.

Conclusion

The MOVPE process requires a source of oxygen-free carrier gas, this can be readily achieved using a palladium-silver membrane diffusion system. In the event of the external (input) surface of diffuser elements becoming oxidised a simple etch in hydrofluoric acid is able to recover the hydrogen flow. The method relies on the conversion of the oxide to a fluoride, which in the case of the silver fluoride hydrate is known to have a high water solubility.

Acknowledgements

"EP–20" hydrogen diffusion units are supplied by Hydrogen Engineering Applications Ltd., Stevenage, Hertfordshire, and incorporate diffusion membranes manufactured by T.M.K.K., Tokyo, using palladium-silver tubes manufactured by Johnson Matthey.

References

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Tungsten-Iridium Alloys at High Temperatures

The benefit of alloying additions of palladium in improving the oxidation resistance of tungsten alloys at elevated temperatures has been reported in this journal recently (1). Now, the enhancement of the high temperature strength of tungsten by alloying with iridium is the subject of a new study at the Arizona State University (2).

The investigators report that dilute alloys containing up to 1 weight per cent iridium in solid solution display considerably enhanced yield and tensile strengths at high temperatures. For a tungsten-0.8 weight per cent iridium alloy, a yield strength improvement of 75 per cent is observed at 1727°C. This gain becomes progressively less marked as the temperature increases towards 2327°C. The incremental strength benefit was found to be linearly dependent on the iridium concentration, consistent with the mechanism of solid solution strengthening by atoms in substitutional positions causing symmetrical lattice distortion. Examination of the fracture behaviour showed that iridium promotes the intergranular failure mode at lower temperatures.

These results demonstrate that iridium is a viable alternative to rhenium as a strengthening alloying element in tungsten. Earlier work by the authors has shown that iridium also improves the fabricability of tungsten at ambient temperatures, and is better than rhenium. Such findings should encourage the use of tungsten-iridium alloys in industrial applications.

C.W.C.

References

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