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Non Wetchemical Lift Off of Titanium Dry Etch Masks by Hydride Formation

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A new non wetchemical method for removal of titanium dry etch masks from InP surfaces has been developed. Lift off of titanium layers on InP is easily achieved by a jet of air or organic solvent, if the samples are heated in neutral H_2-gas or subject to an hydrogen ion beam of relatively low energy.

1. INTRODUCTION

Titanium is a suitable etch mask for ion beam etching of III-V semiconductor materials with the N_2/H_2O gas system. This new gas mixture for deep groove ion beam etching of InP and InGaAsP with titanium mask material was presented at the SSDM '90 conference[1]. This method meanwhile has become a standard process for laser fabrication[2].

However, due to formation of TiO_2 and TiN during the etch process, which are responsible for the extremely low ion beam etch rate of titanium, wet chemical removal of the etch mask without attacking the semiconductor material is somewhat difficult.

Since there is no interfacial reaction between InP and e-gun evaporated titanium up to 350 °C the deliberate formation of strain at the interface can reduce the adhesion and, thus, lead to lift off. The strain generated by a phase transition in the system titanium-hydrogen is sufficient to do that.

2. EXPERIMENTAL PROCEDURES

Titanium layers with thicknesses in the range of 100 to 200 nm were evaporated by an e-gun in a turbomolecular pumped stainless steel chamber. Starting pressure prior to evaporation was $< 5 \cdot 10^{-7}$ Torr, the typical growth rate 2 nm/s. Chemomechanical polished (100)-InP (n, p and s.i.) was used for substrate material without further cleaning steps. After evaporation some wafers were stored under ambient conditions, others were ion beam etched with two different etch gas combinations: Ar/H_2O and N_2/H_2O. Typical beam parameters were:
E_{Beam} = 1000 eV, j_{Beam} = 1 mA/cm^2, the partial pressures amounted to $p_{Ar} = p_{N_2} = 4 \cdot 10^{-5}$ Torr, $p_{H_2O} = 1 \cdot 10^{-5}$ Torr. For laser processing an InP etch

depth of approximately 2,5 µm is desired. At least all 3 types of samples were subject to two different procedures.

1) Hydrogenation in a neutral gas stream: The process sequence consisted of heating up the sample on a graphit boat with 280°/min, holding it at a temperature level of T_L = 330 °C for times t_L up to 10 min and cooling it down to room temperature with a rate of 140°/min. Such a temperature-time behaviour was accomplished by a programmable temperature controller. The surface state of the titanium mask was monitored during this process by measuring the reflected light intensity of a 633 nm He-Ne-laser.
2) Beaming of the sample with hydrogen ions generated by a Kaufmann-type ion source. The working conditions were:
   E_{Beam} = 100 to 500 eV
   j_{Beam} < 50 µA/cm²
   p_{H_2} = 2·1=⁻⁴ Torr
   typical processing time < 20 min.

3. EXPERIMENTAL RESULTS

According to the Ti-H-phase diagram[3),4)], shown partly in Fig. 1, titanium can, depending on temperature and holding time, solve up to 8 at % hydrogen in its hexagonal α-phase. During cooling down the sample from a point in the α-region the phase boundary is crossed into a two phase region: (α + γ), where the γ-phase is of body centered cubic lattice type with hydrogen solved in the tetrahedral interstices.

Fig. 2 shows the blistery surface of a titanium layer on InP after such an hydrogenation and cooling process. The sudden change of the titanium surface from mirrorlike reflection to diffuse scattering allows the exact determination of the transition temperature with a photometer (Fig. 3). Fig. 4 shows the resulting transition temperatures ϑ_p for different holding times for unetched and Ar/H_2O etched samples at a holding temperature of 330°C. The increase of the transition temperature with increasing holding time is a consequence of the form of the $\alpha/(\alpha + \gamma)$-phase boundary.

Despite the saturation effect of ϑ_p for $t_L \geq 5$ min there is no indication for a horizontal(T_L = const) phase transition which should occur for a prolonged loading time. Perhaps the Ti-H phase diagram which was investigated on bulk material, is only qualitatively applicable to the case of thin films. The different behaviour of unetched and Ar/H_2O samples is due to a different velocity of H_2-indiffusion. Despite the fact of an approximately 50 % thicker oxid layer in the etched sample[5)], which should have a retarding effect the indiffusion of H_2 is much faster due to the presence of lattice vacancies generated in the etch damaged part of the layer. The behaviour of N_2/H_2 ion etched samples prooved to be completely different. They didn't become blistery across the surface when treated with neutral hydrogen. Obviously the oxinitride layer, present on the titanium film, acts as a diffusion barrier for hydrogen. This assumption is supported by the fact, that samples cleaved after ion etching show effects starting at the

freshly opened titanium sidewall areas (Fig. 5).

To overcome this diffusion barrier the samples must be beamed with energetic ions of a Kaufmann-type ion source (E_{Beam} 100 - 500 eV) which leads to blistering surfaces as in the preceding cases. Fig. 6 shows a laser structure after N_2/H_2O ion etching and hydrogen beaming, Fig. 7 the same structure after blowing off the lifted titanium layers.

4. CONCLUSION

A new non wetchemical method to remove titanium etch masks from InP has been developed. As the processing temperature can be held well below 350 °C (where InP starts to decompose even in pure hydrogen atmosphere) there is no detrimental influence of the titanium on the underlying InP material. Changes in the carrier concentration of n- or p-doped InP substrate material due to hydrogen ions can be cured by short time annealing at temperatures < 350 °C.

5. REFERENCES

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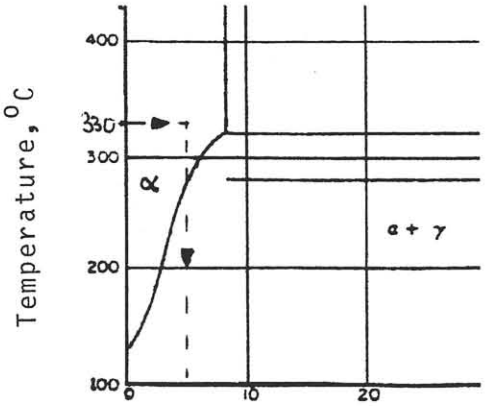

Fig.1: Ti - H phase diagram (detail)

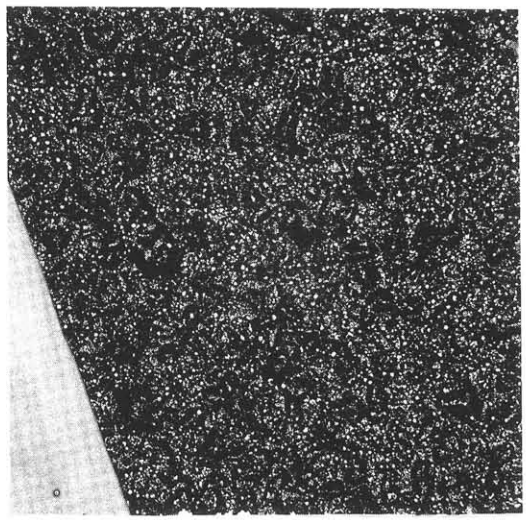

Fig.2: Blistered titanium layer on InP substat

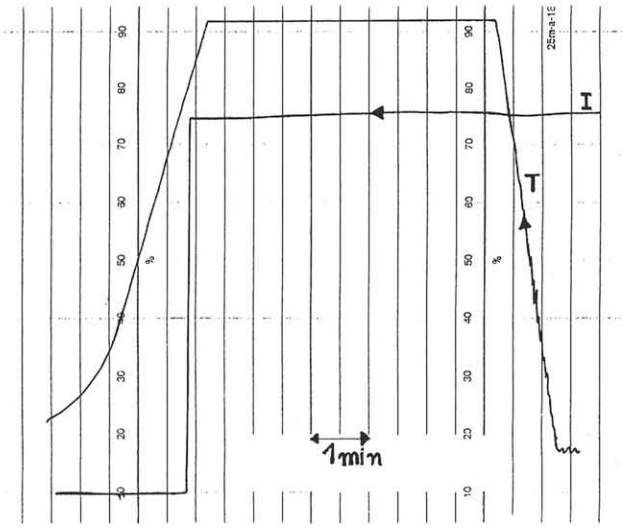

Fig.3: Sample temperature T and reflected laser intensity I as function of time during a hydrogenation process

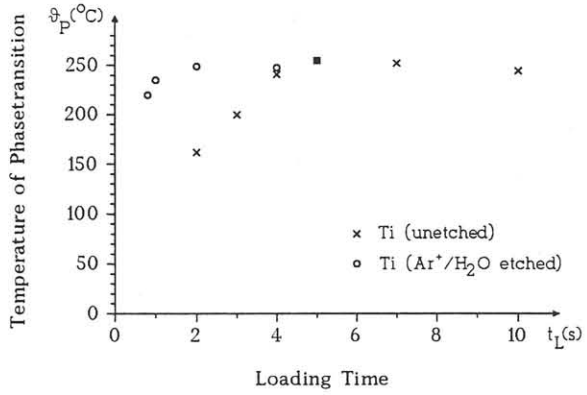

Fig.4: Influence of hydrogen loading time on the phase transition of titanium

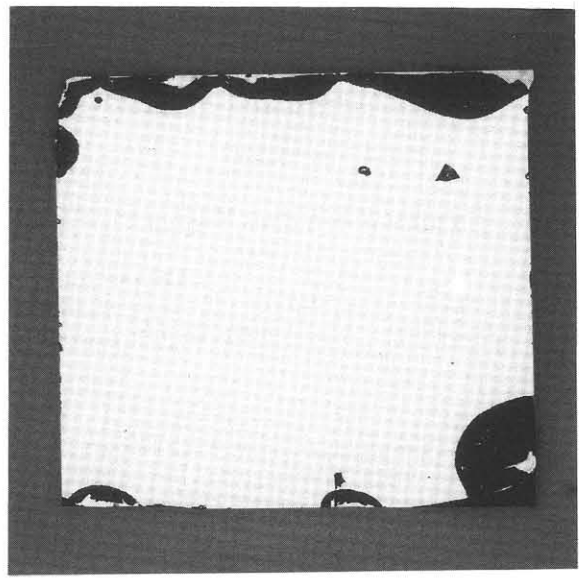

Fig.5: N_2/H_2O ion etched sample after hydrogenation

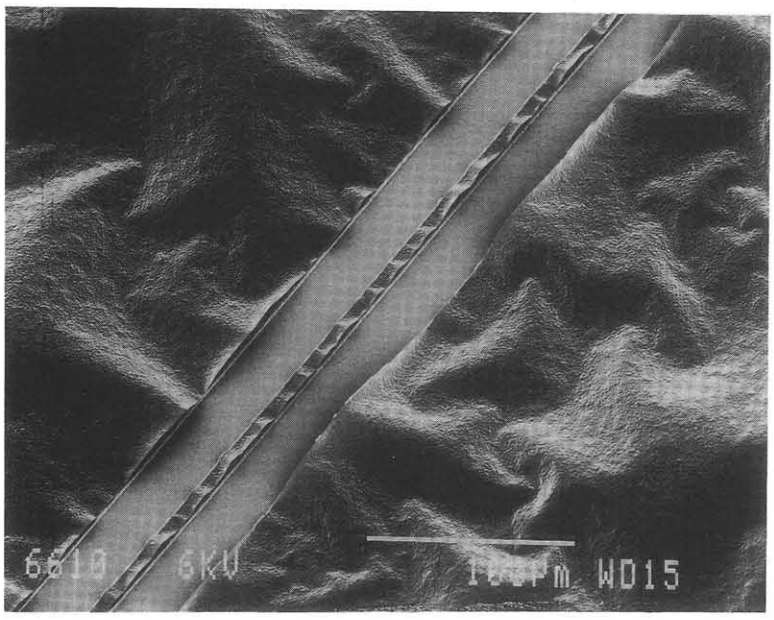

Fig.6: Titanium masked N_2/H_2O ion beam etched laser structure after hydrogen ion beaming

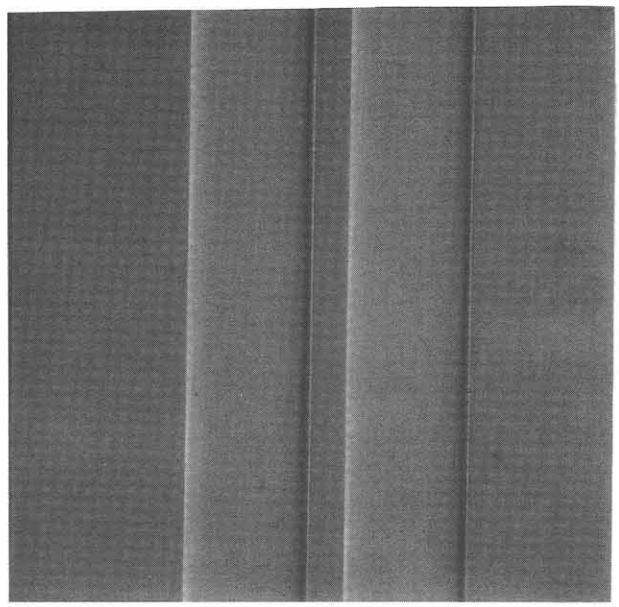

Fig.7: Structure of Fig.6 after organic solvent jet treatment