JOURNAL OF MATERIALS SCIENCE 23 (1988) 2761–2767

Chemical thinning of III–V compound semiconductors for transmission electron microscopy

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A vapour jet etching method and suitable equipment are tested in order to thin monocrystalline and polycrystalline material of GaAs, InP and InAs for transmission electron microscopy. The reactive vapour jet consists of air, bromine and methanol. The thinning procedure is monitored by an optical microscope. Large thin areas could be obtained using a bubbler temperature of 60° C, 20% bromine in methanol, a distance between nozzle and sample surface of 1.5 mm and a nozzle mouth diameter of 0.7 mm. During pre-etching the vapour flow rate was 0.7 l min^{-1}, and 0.3 l min^{-1} was realized during final etching up to perforation. The etching times ranged between 1 to 2 min with an initial sample thickness of 350 to 365 μm. Large thin areas have only been obtained using an excentric position of the nozzle with respect to the sample centre in combination with a manual rotation of the specimen holder.

1. Introduction

Much work has been done on the preparation of thin foils of metals, oxides, elemental semiconductors and III–V compound semiconductors by chemical jet thinning, electropolishing, dipping techniques and ion-milling [1–6]. During the last few years the ion-thinning techniques have attracted preferential interest in the preparation of cross-sectional specimens of homo- and hetero-epitaxial multilayer structures (e.g. [7–15]). However, the chemical thinning methods have not lost their attractiveness because of their simplicity with respect to the equipment and their high rates of material removal. Extensive reviews on the usual etchants and methods for chemical polishing and thinning of GaAs and GaP are given in the literature [4–6]. No additional fundamentally new chemical methods have been developed up to now for GaAs and GaP thinning. The well-known recipes and methods reported in the literature [4–6] have been slightly modified and they have also been applied to mixed-compound semiconductors, InP, InAs and so forth. Table I gives some additional reviews on GaAs, InP, InAs, GaP, InSb and GaSb. From Table I it follows that a solution of bromine in methanol is one of the most useful etchant for the III–V compound semiconductors. Recently, Aytac *et al.* [52] have tested a new solution consisting of HCl, HNO_3, $HClO_4$ and CH_3COOH of various mixing ratios for thinning InP by a modified chemical thinning technique. The aim of this paper is to present a modified jet etching method and a simple thinning device (similar to [17]) for the preparation of monocrystalline and polycrystalline samples of GaAs, InP and InAs for transmission electron microscopy. On the other hand this method and equipment were used to produce well-defined etch pits on (0 0 1) InP which are suitable for the distinction of the [1 1 0] and [$\bar{1}$ 1 0] directions [53].

2. Experimental procedure

The distinction of the method presented here compared with other usual jet thinning techniques is that the etchant attacking the sample surface does not consist of a liquid but of a vapour composed of bromine, methanol and air. The advantage of this method compared with the dipping technique is that the extremely high etching rates usual for jet methods remain preserved. On the other hand the mechanical loading of the thin sample areas seems to be considerably less than during jet thinning using a liquor. Fig. 1 shows schematically the experimental arrangement and Fig. 2 the thinning device in detail. Using a water-jet vacuum pump ((10) in Fig. 1), air is sucked through the input (1). This air, passing a flow-meter (3), spouts through a bubbler (4) filled with a solution of bromine in methanol. It is important to achieve a temperature variation of this bromine–methanol solution. The bromine–methanol–air vapour streams through a nozzle mouth (0.7 mm in diameter) against the sample. During etching the vapour is sucked off continuously by the water-jet vacuum pump. The nozzle device, consisting of a wide quartz pipe, enables the illumination and direct visual inspection of the sample by the microscope (8) during the etching procedure. The sample (3 mm in diameter) is positioned in a Teflon holder a small distance (x) from the nozzle mouth. The flowthrough of air and therefore the vapour jet too are controllable by a throttle (2).

3. Results and discussion

In order to realize high etching rates the distance

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TABLE I Usual recipes and methods for thinning III–V compound semiconductors

Material	Orientation	Agent	Method*	Ref.
GaAs	(0 0 1)	$HNO_3:HF:HCl:H_2O = 6:2:1:5$	D with specimen rotation	[16]
GaAs	(0 0 1)	$HCl:H_2O_2:H_2O = 40:4:1$	J	[17]
GaAs	(0 0 1)	Br_2–CH_3OH	J	[18]
GaAs	{1 1 1}	NaOH aqueous solution with 1% available Cl_2	EJ	[19]
$Ga_{0.6}Al_{0.4}As$	(0 0 1)	$H_2SO_4:H_2O_2:H_2O = 10:1:1$		[20]
$GaAs_{0.5}P_{0.5}$	(0 0 1)	15 drops Br_2 in 100 ml CH_3OH	J	[21]
$Ga_{0.9}Al_{0.1}As$	(0 0 1)	$H_2O:NH_4OH = 10:1$	As [16]	[22]
GaAs	(0 0 1), {1 1 1}	15% Br_2 in CH_3OH and perchloric acid with 75% glacial acetic acid	EJ	[24]
$Ga_{0.7}Al_{0.3}As$ GaAs $In_{0.53}Ga_{0.47}As$	(0 0 1), $(\bar{1}\bar{1}\bar{1})$	$HNO_3:HCl = 1:3$	D at 50 to 60° C	[25]
GaAs, InAs, InSb, GaSb and InP	{1 1 1}	Mixtures of acids with water; Br_2 in CH_3OH	After [23]	[26]
GaP	{1 1 1}	$HCl:HNO_3 = 1:1$	J	[19, 27]
GaP	(0 0 1)	$HCl:HNO_3 = 3:1$	D at 50 to 60° C	[28]
GaP	$(\bar{1}\bar{1}\bar{1})$	Cl_2 in CH_3OH	D	[29]
GaP	$(\bar{1}\bar{1}\bar{1})$	Cl_2 in CH_3OH	J after [17]	[30]
GaP	(1 1 1)	1% NaOH solution	EJ	[31]
GaP	{1 1 1}	$HCL:HNO_3 = 3:1$ or $HNO_3:HCl:H_2O = 5:1:1$	D at 30 to 40° C	[32]
InAs		$HNO_3:HCl = 1:1$	D after [33]	[34]
InP	(0 0 1)	$HCl:HNO_3 = 1:1$	D	[35]
InP	(0 0 1), $(\bar{1}\bar{1}\bar{1})$, (1 1 0) cross-section	Br_2 in CH_3OH	D, J	[36–43]
InP	(0 0 1)	Cl_2 in CH_3OH	D, J	[44–46]
InGaAsP	(0 0 1)	Br_2 in CH_3OH		[47]
InGaAsP and InGaAs	(0 0 1)	Cl_2 in CH_3OH	J	[48]
InP/InGaAs, InP/InGaAsP	A special (1 1 0) cross-section preparation technique (final thinning by dipping in a 0.5% Br_2–methanol solution)			[49, 50]
InP	(0 0 1)	$HCLO_4$: $HCl:HNO_3:CH_3COOH$ of various mixing ratios	D at 60° C	[52]
GaAs	(0 0 1)	Cl_2 in CH_3OH	J after [44]	[51]

*D = dipping techniques, J = jet thinning, EJ = electrochemical jet thinning, E = electrochemical polishing.

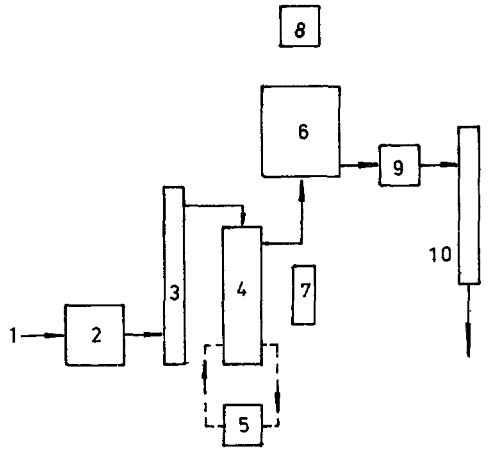

Figure 1 Schematic representation of the equipment: (1) air input, (2) throttle, (3) flow meter, (4) bubbler, (5) thermostat, (6) thinning device, (7) lamp, (8) optical microscope, (9) valve, (10) water-jet vacuum pump.

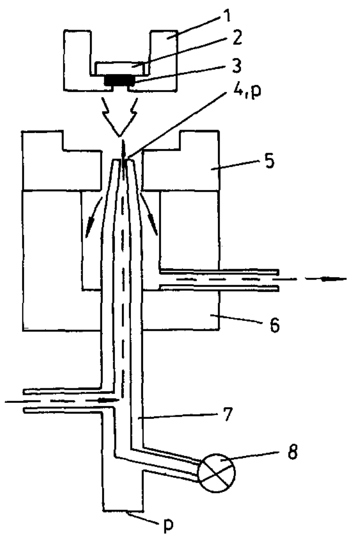

Figure 2 Thinning device in more detail: (1) specimen holder, (2) glass wafer, (3) sample, (4) nozzle mouth (p = polished), (5) Teflon cover, (6) Teflon box, (7) quartz nozzle, (8) valve.

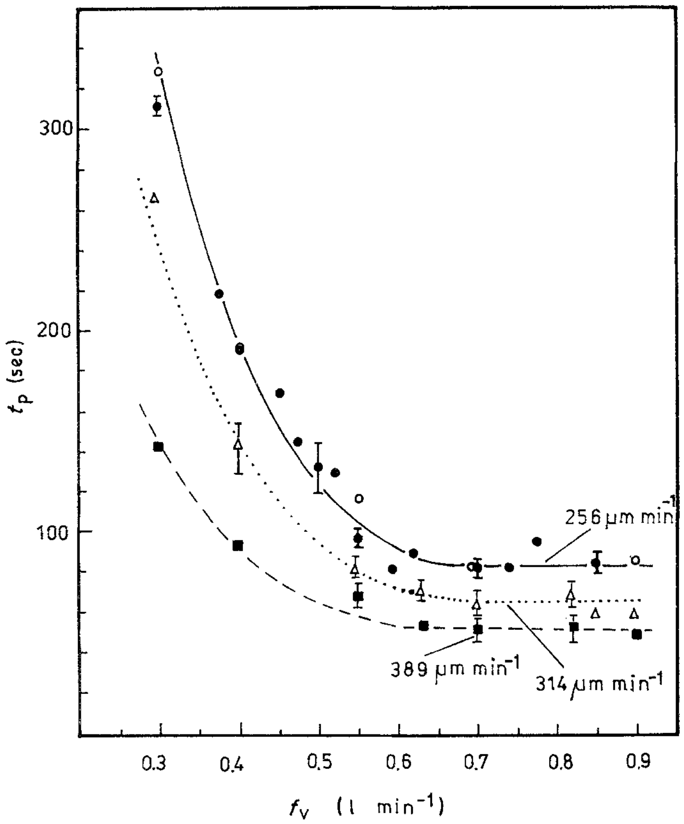

Figure 3 Relationship between time up to perforation t_P and flow rate f_v for GaAs (dopant Te). t = 350 μm, x = 1.5 mm. The nozzle is located centrically with respect to the sample centre; no rotation of the specimen holder. (●) (0 0 1), T_B = 40° C, 10% bromine in methanol; (○) ($\bar{1}\,\bar{1}\,\bar{1}$), 40° C, 10%; (△) (0 0 1), 40° C, 20%; (■) (0 0 1), 60° C, 20%.

x between nozzle mouth and specimen surface was kept preliminarily at 1.5 mm. During the following experiments the nozzle mouth was always 0.7 mm in diameter. Differently oriented GaAs and InP monocrystalline wafers (3 mm in diameter) variously doped were used for experiments. Additionally polycrystalline InP, GaAs and InAs material grown by the Bridgman method have been tested. Figs 3 and 4 depict the dependences of the etching time t_P up to perforation on the vapour flow rate f_v for two different bubbler temperatures T_B, various concentrations of bromine in methanol and for a constant sample thickness t (t_{GaAs} = 350 μm, t_{InP} = 365 μm). Generally, in the range $0.3 < f_v < 0.6$ l min^{-1} the etching rate r increases exponentially with increasing f_v for both GaAs and InP. With $f_v > 0.6$ l min^{-1} the etching rates are constant but different for the various etching parameters listed in Figs 3 and 4. It was found that the etching rates of the orientations (0 0 1) and ($\bar{1}\,\bar{1}\,\bar{1}$) are the same. In the case of GaAs the etched

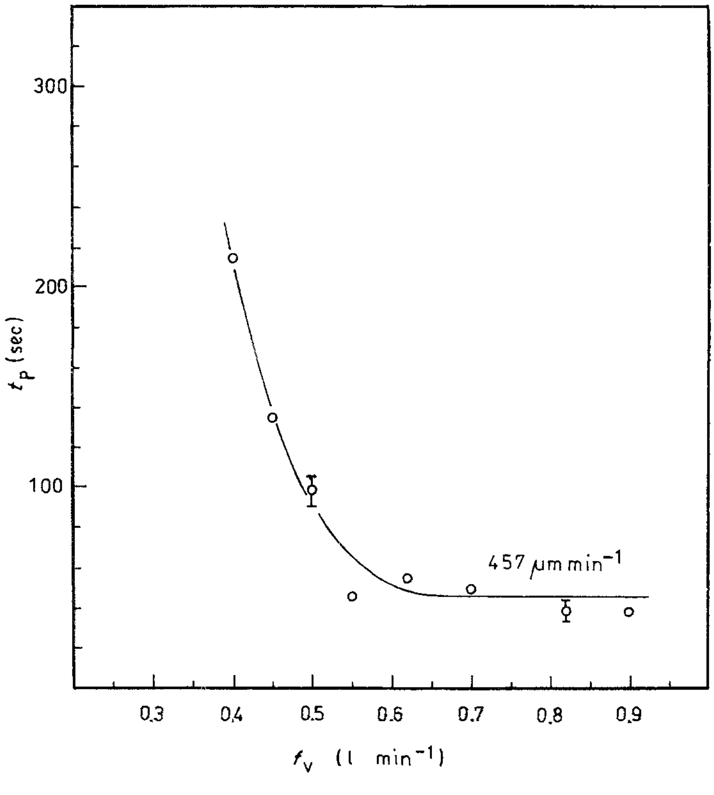

Figure 4 Dependence of t_P upon the flow rate f_v for (0 0 1) InP (dopant Sn). t = 365 μm, x = 1.5 mm. Nozzle position as in Fig. 1. T_B = 60° C, 20% bromine in methanol.

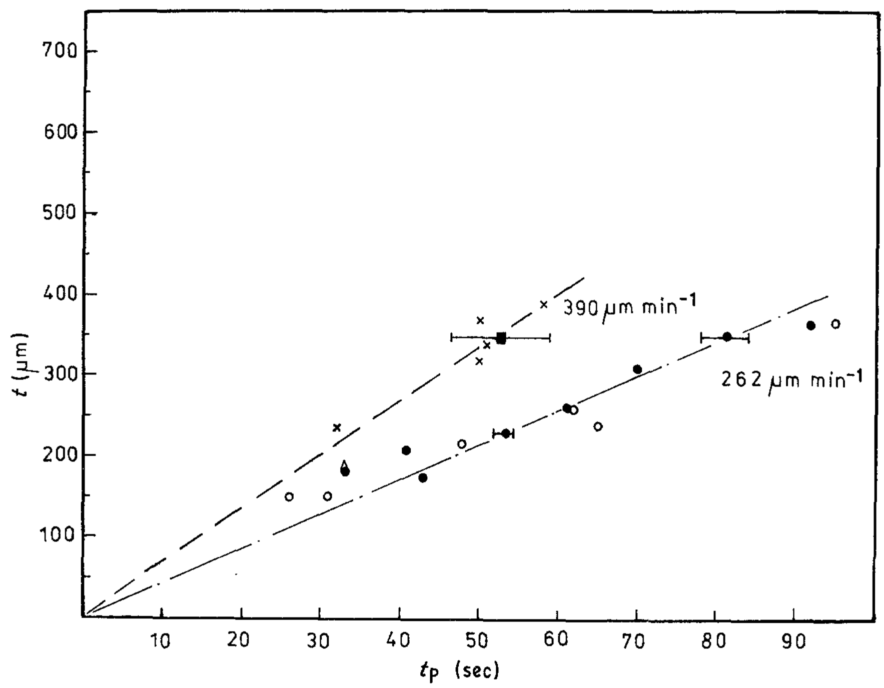

Figure 5 Dependence of removed thickness t against t_P for GaAs. Central nozzle position, non-rotating sample, $f_v = 0.71\,\mathrm{l\,min^{-1}}$, $x = 1.5\,\mathrm{mm}$. (x) Polycrystal, T_B = 60° C, 20% bromine in methanol; (■) (0 0 1), dopant Te, T_B = 60° C, 20% bromine in methanol; (●, ○, △) (0 0 1), dopants Te, Sn and Cr respectively, T_B = 40° C, 10% bromine in methanol.

surfaces are smooth over the whole range of f_v with $T_B = 60°\,\mathrm{C}$, 20% bromine in methanol, $x = 1.5\,\mathrm{mm}$ and $d = 0.7\,\mathrm{mm}$ (d = nozzle mouth diameter). For $f_v < 0.31\,\mathrm{l\,min^{-1}}$ the InP surfaces are rough. Above $f_v \approx 0.31\,\mathrm{l\,min^{-1}}$ the InP sample surfaces are smooth too, but well-defined etch pits at dislocations are formed. With a continuous increase of f_v the tendency to etch-pit formation is quickly reduced (see also [53]). It was not possible to thin GaAs and InP samples of the orientation (1 1 1).

Figs 5, 6 and 7 show the linear change of t_P with specimen thickness t for variously doped (0 0 1) GaAs, (0 0 1) InP and polycrystalline material for GaAs, InP and InAs for different thinning parameters given in the figures. The parameters x and f_v were kept constant at 1.5 mm and $0.71\,\mathrm{l\,min^{-1}}$, respectively. The slopes of the straight lines yield the etching rates $r = \mathrm{d}t/\mathrm{d}t_P$. From the linear dependence of t_P upon t, usual for high flow rates, it follows that transport of reaction products is not hindered inside the thinned hollow at such high flow rates when the etch depth is increased with time more and more. Both the dopant and orientation used do not have an influence on the etching rate. However, if the number of grains with the (1 1 1) orientation parallel to the sample surface is less within polycrystalline material, then the etching rate is the same too. Comparing the etching rates from Figs 3 to 7 it is observed with $f_v = 0.71\,\mathrm{l\,min^{-1}}$ that $r_{\mathrm{InAs}} > r_{\mathrm{InP}} > r_{\mathrm{GaAs}}$ at comparable etching conditions. With increasing distance x between nozzle mouth and sample surface the etching rate decreases linearly within the x-range from 1.5 to about 6 mm (Fig. 8). Afterwards the time up to perforation t_P increases exponentially when x is increased. This is due to

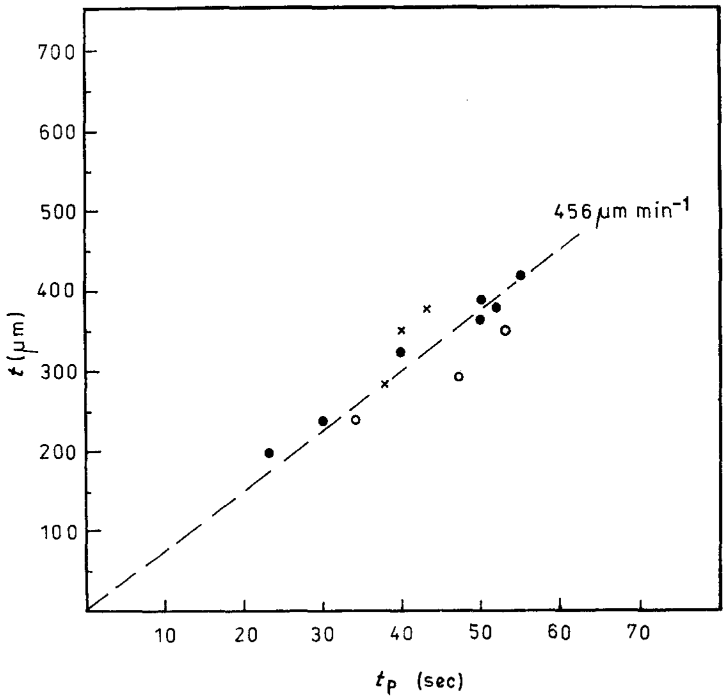

Figure 6 As Fig. 5, for InP (dopant Sn). $f_v = 0.71\,\mathrm{l\,min^{-1}}$, $x = 1.5\,\mathrm{mm}$, T_B = 60° C, 20% bromine in methanol. (●) (0 0 1), (x) ($\bar{1}\,\bar{1}\,\bar{1}$), (○) undoped polycrystal.

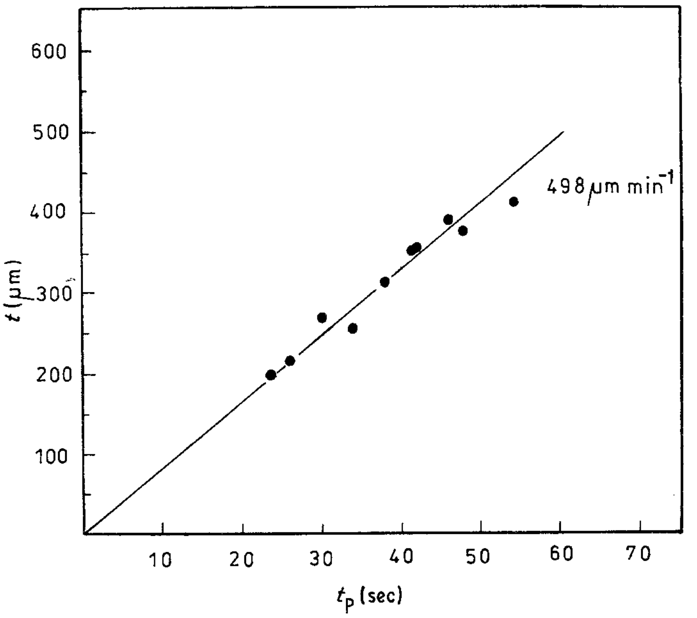

Figure 7 As Fig. 5, for polycrystalline InAs (undoped polycrystal). $f_v = 0.71\,\text{min}^{-1}$, $x = 1.5\,\text{mm}$, $T_B =$ 60° C, 20% bromine in methanol.

the construction of the device. With increasing x the transmittable areas become a little larger. However, due to the very small nozzle mouth diameter of 0.7 mm the thin areas suitable for TEM are much smaller because of the very steep walls of the hollows thinned.

Thinning experiments using a nozzle having a mouth of 2.7 mm revealed that no polishing effect occurred because of the rapid decay of r when f_v, T_B, bromine concentration and x were kept constant at $0.71\,\text{min}^{-1}$, 60° C, 20% and 1.5 mm, respectively. Therefore the nozzle with $d = 0.7$ mm was positioned excentrically with respect to the specimen centre (Fig. 9). A continuous manual rotation of the specimen holder gives rise to very large transmittable sample areas using the experimental conditions mentioned above. It is noticed that in the case of monocrystalline material the time up to perforation is increased by a factor of 1.5 for GaAs and 1.7 for InP when the specimen holder is turned and the nozzle is positioned excentrically with respect to the sample centre (Fig. 10). Fig. 9 shows schematically the results obtained with and without sample rotation. However, according to Fig. 10 the etching rates remain extremely high. To obtain a better control of the moment of perforation or transparency it is more favourable to decrease the flow rate of about $0.3\,\text{l}\,\text{min}^{-1}$ a short time before perforation. Then, only in the case of InP were well-defined etch pits found on the sample surface thinned. Their size increased with increasing etching time when $f_v = 0.3\,\text{l}\,\text{min}^{-1}$. After or shortly before perforation (for examples see Fig. 11) the specimen holder containing the sample is removed quickly from the thinning device. It is then rinsed with clean methanol and water. For these conditions the thin sample areas are appreciably larger than without sample rotation. Some thinning tests with GaAs and InP of the (1 1 0) orientation have also provided samples acceptable for TEM.

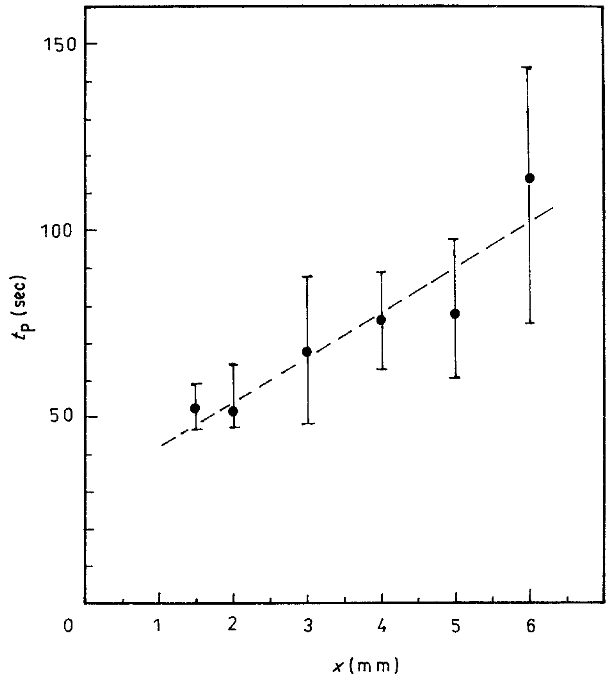

Figure 8 The time up to perforation t_P of a 350 μm thick (0 0 1) GaAs sample (dopant Te) upon the distance x between nozzle and sample surface. $f_v = 0.71\,\text{min}^{-1}$, $T_B = 60°\,\text{C}$, 20% bromine in methanol.

4. Summary

It is possible to obtain monocrystalline and polycrystalline specimens of GaAs, InP and InAs for TEM

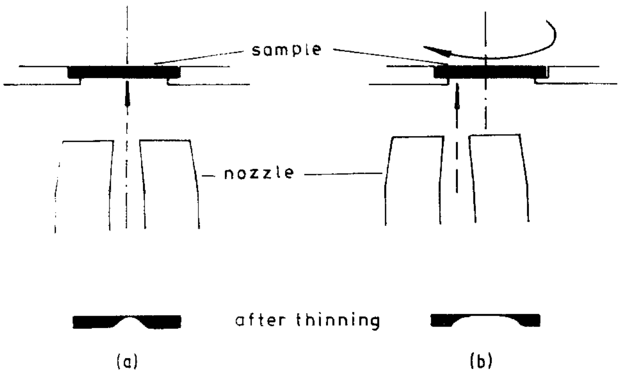

Figure 9 Schematic diagram of arrangements and results of thinning: (a) non-rotating sample, (b) rotating sample with excentric nozzle position.

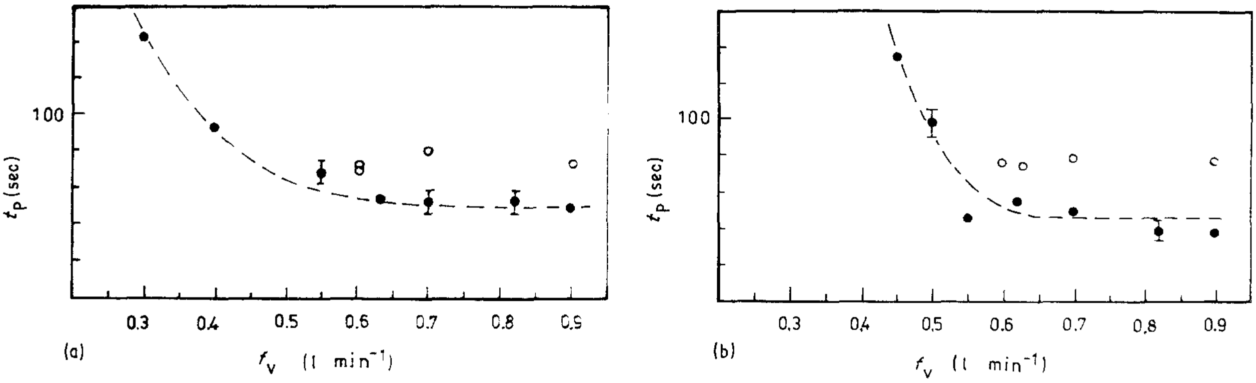

Figure 10 Decrease of etching rate $r = \mathrm{d}t/\mathrm{d}t_\mathrm{P}$ for (0 0 1) samples of (a) GaAs : Te with $t = 350\,\mu$m and (b) InP : Sn with $t = 365\,\mu$m. (○) Nozzle arrangement shown in Fig. 9b; (●) arrangement shown in Fig. 9a. $T_\mathrm{B} = 60°$C, 20% bromine in methanol, $d = 0.7$ mm, $x = 1.5$ mm.

examinations by a jet thinning procedure using a vapour mixture of air, bromine and methanol as the reactive etchant. The best conditions are: $T_\mathrm{B} = 60°$C, 20% bromine in methanol, $x = 1.5$ mm, $d = 0.7$ mm, f_v (pre-etching) $= 0.7\,\mathrm{l\,min^{-1}}$, f_v (final etching) $= 0.3\,\mathrm{l\,min^{-1}}$, an excentric position of the nozzle mouth with respect to the sample centre and using a manual rotation of the specimen holder. Under these conditions large sample areas could be produced suitable for TEM. Mixed semiconductors such as InGaAs, InGaAsP and GaAsP can be thinned by means of this method too. It is not possible to thin GaP when a vapour jet of air, bromine and methanol is used.

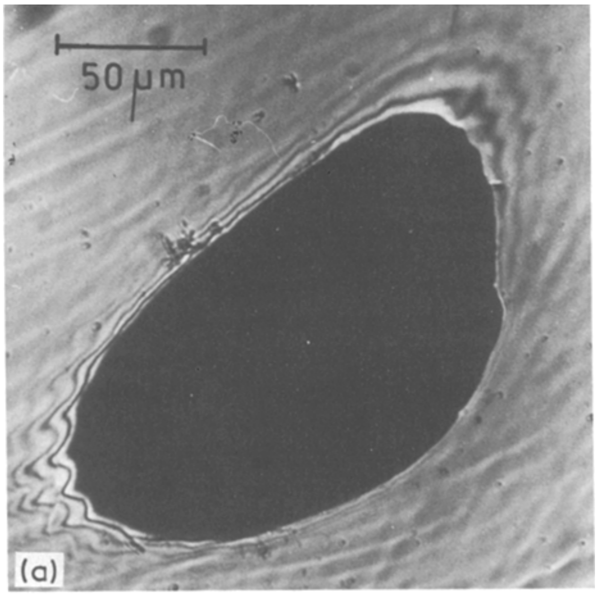

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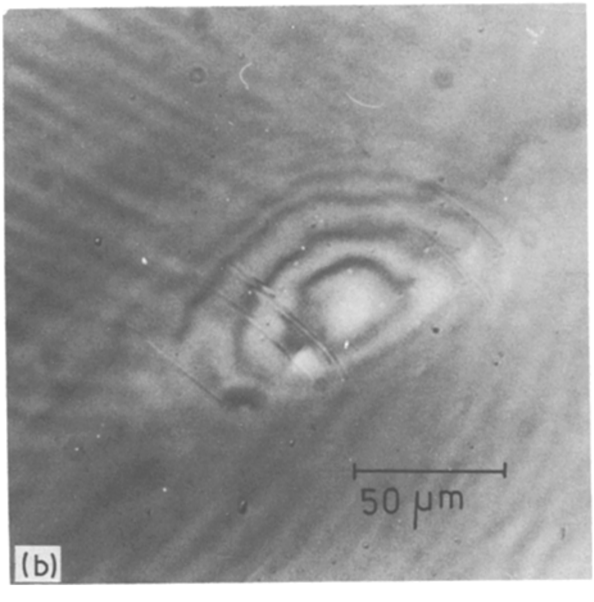
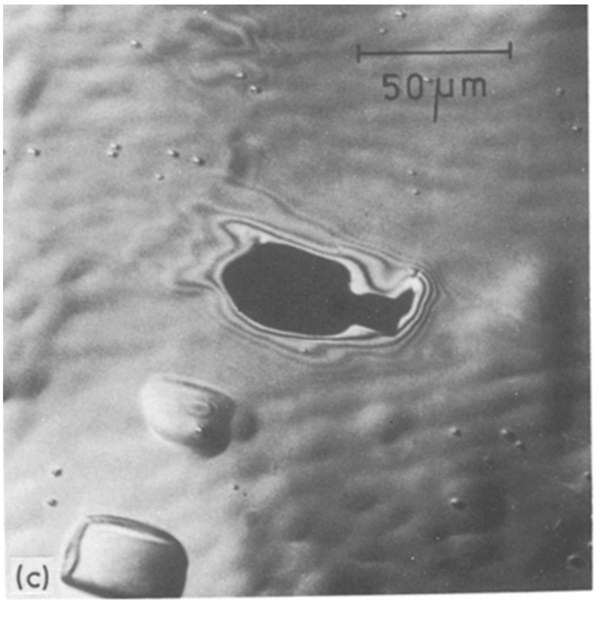
Figure 11 Optical micrographs of thinned samples obtained using nozzle position shown in Fig. 9b. Experimental conditions: $T_\mathrm{B} = 60°$C, $x = 1.5$ mm, $d = 0.7$ mm, 20% bromine in methanol, f_v (pre-etching) $= 0.7\,\mathrm{l\,min^{-1}}$, f_v (final etching) $= 0.3\,\mathrm{l\,min^{-1}}$. (a) (0 0 1) GaAs : Te after perforation, sample thickness $t = 350\,\mu$m, time of pre-etching about 50 sec. (b) (0 0 1) GaAs : Te some seconds prior to perforation. (c) (0 0 1) InP : Sn after perforation, sample thickness 365 µm, time of pre-etching about 45 sec; note small well-defined dislocation etch pits.





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Received 23 July
and accepted 26 November 1987