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A STUDY OF THERMODYNAMIC PHASE STABILITY OF INTERMETALLIC THIN FILMS OF Pt_2Ga, PtGa AND $PtGa_2$ ON GALLIUM ARSENIDE

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ABSTRACT

Epitaxial thin films of three different Pt-Ga intermetallic compounds have been grown on GaAs by molecular beam epitaxy (MBE). The resultant films have been annealed at various temperatures and then examined using X-ray two-theta diffraction. Both $PtGa_2$ and PtGa thin films are chemically stable on GaAs under 1 atmosphere of N_2 up to 450°C and 600°C, respectively. Thin films of Pt_2Ga react with GaAs at temperatures as low as 200°C to form phases with higher Ga concentration.

Introduction

The interface chemistry of metal-semiconductor contacts plays an important role in controlling the electrical properties of Schottky barriers and Ohmic contacts [1]. Chemically stable contacts must be formed at the metal-semiconductor interface in order for electronic devices to survive processing procedures and operate reliably in harsh environment applications for long periods of time [2,3]. A possible solution for this interface problem would be to use a contact metal that can coexist with GaAs in bulk thermodynamic equlibrium. Such stable metals can be found by examining ternary phase diagrams, such as the Pt-Ga-As system, which was experimentally elucidated by Tsai et. al. [4] and is illustrated in Fig. 1. The existence of a pseudobinary tie-line between two compounds in the ternary phase diagram implies that the compounds will not react with each other in a closed system, i.e. the bulk compounds are in thermodynamic equilibrium with respect to each other. Therefore, from Fig. 1 it can be expected that PtGa and $PtGa_2$ will form stable contacts with GaAs but that Pt_2Ga will not. In the present study, these expectations are tested by investigating the phase composition of thin films of Pt_2Ga, PtGa and $PtGa_2$ on GaAs after annealing to various temperatures.

Film Growth

The Pt-Ga intermetallic films were grown in a MBE chamber with a base pressure of 2×10^{-10} torr and a deposition pressure of approximately 4×10^{-9} torr. The two inch GaAs substrates were introduced via a cryopumped load lock system and mounted on a modified manipulator equipped with radiative heating elements. The samples were cleaned in-situ by heating to a temperature of approximately 525°C. The platinum was evaporated using a Varian 3 KW electron beam evaporator and the gallium was obtained from a Knudsen cell constructed of a pyrolytic boron nitride (PBN) crucible with a tantalium heating element. The fluxes of platinum and gallium were initially tuned to the proper stoichiometry based on empirical knowledge. $PtGa_2$ can be visually identified by its characteristic golden color, since $PtGa_2$ is the only Pt-Ga phase that has a band structure similar to that of elemental gold [5]. Neither PtGa nor Pt_2Ga can be easily identified by color. The flux rate from the gallium source was stabilized by temperature control circuits that ensured a constant flux rate for each source power setting. Subsequent depositions have been controlled with a Leybold-Inficon IC-6000 crystal monitor system. To obtain single phase Pt-Ga intermetallic films, the flux ratio of gallium to platinium was adjusted to be slightly Ga rich. Co-evaporation of each Pt-Ga intermetallic proceeded with the substrate held at temperatures ranging from near room temperature to over 500°C at epilayer growth rates ranging from approximately 0.5 to 5 microns/hour.

Composition Analysis

XRD patterns of the films were taken on a Phillips X-ray powder diffractometer, which was interfaced to a microcomputer that controlled the scan rate and collected data at 0.1° intervals with a counting time of 10 seconds at each angle. The total time required for a complete scan (2θ from 10° to 100°) was about 3 hours and the typical signal-to-noise ratio for a strong diffraction peak was 30 to 1. The d spacings of the $PtGa_2$ and Pt_2Ga thin films were checked against a reference tabulation [6] to ensure that they were identified correctly. As no known PtGa JCPDS data exists, the known d-spacings of PtGa [7] were compared with values calculated from the diffraction pattern of the thin film and were found to agree closely. The thin films were annealed for twenty minutes in a quartz tube furnace under a nitrogen atmosphere for temperatures ranging from 100°C to 800° C. In this paper, we present XRD results of annealing studies of the Pt-Ga intermetallic single phase thin films. A complete characterization of these films, including Auger electron spectroscopy (AES) and X-ray photoemission spectroscopy (XPS), will be presented elsewhere [8].

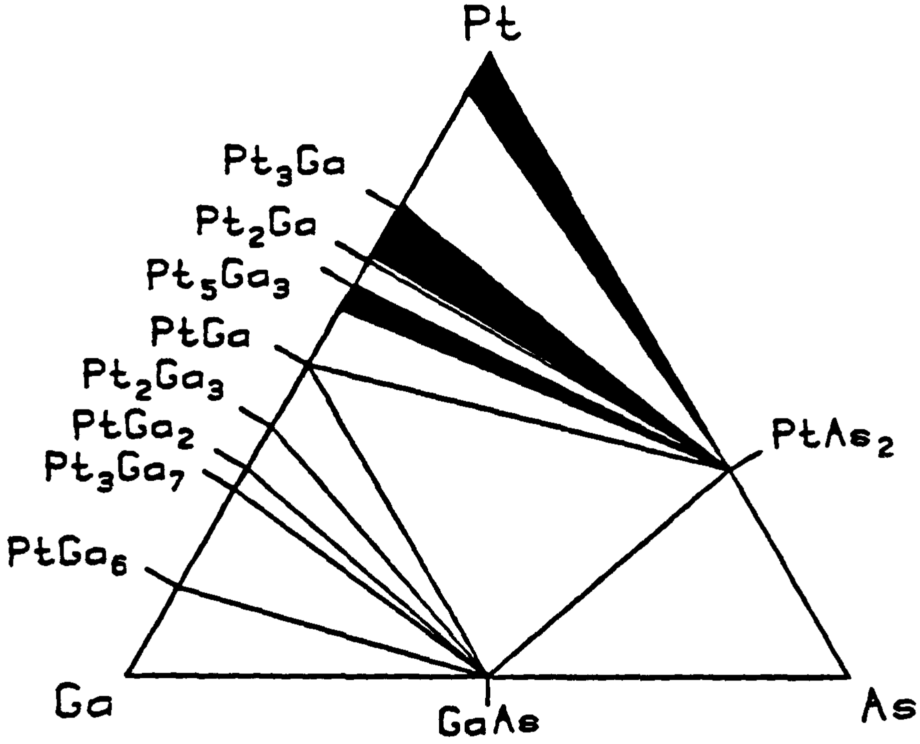

Fig. 1. Solidus portion of the Pt-Ga-As ternary phase diagram at 25°C.

Results and discussion

The grown films were specular, both to the eye and by optical microscopy. Fig. 2 shows typical powder XRD patterns of the three types of intermetallic single phase Pt-Ga thin films grown on GaAs (001) in the as-deposited state. The PtGa and Pt_2Ga thin films have a dominant (210) and (112) reflection, respectively. The $PtGa_2$ thin films displayed roughly equal intensity (111), (220) and (311) reflections. This would seem to imply that the crystal quality of PtGa and Pt_2Ga thin films is better than that of $PtGa_2$ films in spite of larger lattice mismatches. XRD patterns of a sample of Pt_2Ga on GaAs annealed to 500°C are shown in Fig. 3. Even at 200°C, a new peak corresponding to the PtGa (210) reflection begins to appear at $2\theta = 41.4°$. In the diffraction patterns of the film heated to high temperatures, new phases, such as $PtGa_2$ and $PtAs_2$, begin to form at 300°C and all peaks corresponding to the Pt_2Ga phase eventually disappeared at 500°C. According to the Pt-Ga-As ternary phase diagram, Pt_2Ga is expected to react with GaAs to produce $PtAs_2$ and PtGa, because there is no tie-line between Pt_2Ga and GaAs. However, annealing in an open system may cause As evaporation resulting from thermal decomposition of $PtAs_2$ and GaAs. With further loss of As, other Pt-Ga intermetallic compounds, such as $PtGa_2$ and Pt_3Ga_7, may be produced. This prediction agrees very well with the experimental results; all the peaks correspond to PtGa, $PtGa_2$, Pt_3Ga_7 and $PtAs_2$ in the diffraction pattern of the Pt_2Ga thin films on GaAs annealed to 500°C.

Fig. 4 shows XRD patterns of PtGa on a GaAs sample in the as-deposited state and after annealing at various temperatures for 20 minutes each. The diffraction pattern of the PtGa film annealed to 200°C shows that a small peak corresponding to Pt_2Ga (112) beside the PtGa (210) disappeared and the other PtGa peaks became sharper and more intense. This implies that a small amount of unstable Pt_2Ga phase in the PtGa thin film reacted with extra Ga in the film or with the substrate. Annealing improves the crystallinity of the PtGa

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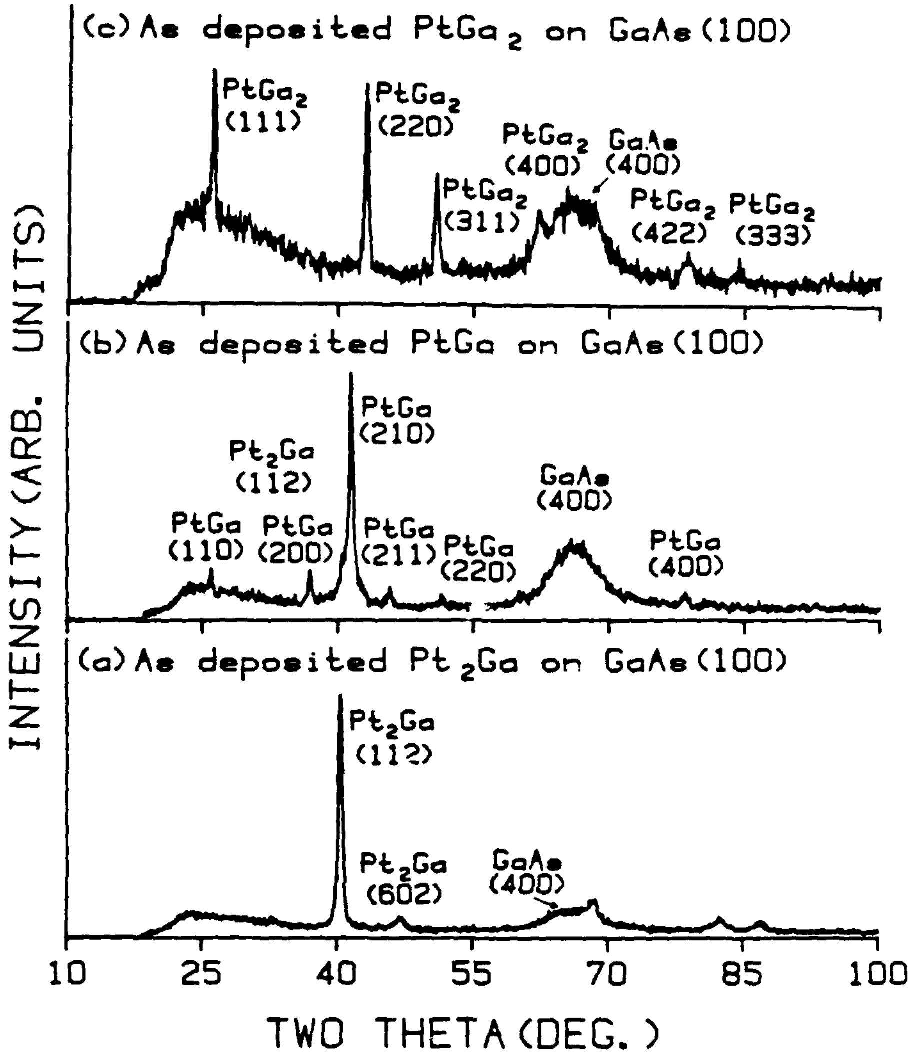

Fig. 2. XRD patterns of the three types of intermetallic single phase Pt-Ga thin films grown on GaAs (100) in the as-deposited state: (a) as-deposited Pt_2Ga on GaAs; (b) as-deposited PtGa on GaAs; (c) as-deposited $PtGa_2$ on GaAs.

film, since the signal-to-background ratio in the XRD patterns begins to increase as annealing temperature goes up. The diffraction patterns for the PtGa film annealed from 300°C to 600°C were essentially identical, but the signal-to-background ratio began to decrease. Annealing in an open system, such as in vacuum or under inert gas, may cause both $PtAs_2$ and GaAs to decompose thermally to produce gas phase As species. Therefore, in this case, the PtGa thin film starts to become Ga rich and $PtGa_2$ and Pt_3Ga_7 are produced, which coexist with PtGa and GaAs. Fig. 5 shows XRD patterns of a sample of $PtGa_2$ on GaAs heated to 100°C, 300°C, 450°C and 500°C, respectively, along with the pattern of an as-deposited film. The diffraction patterns for the sample were essentially identical up to 400°C. A new peak corresponding to the Pt_3Ga_7 (322) reflection begins to appear in XRD patterns of the sample annealed in the range of 450°C to 500°C. It is possible the $PtGa_2$ phase begins to react with extra Ga due to As evaporation from GaAs upon annealing.

Conclusions

Single phase thin films of Pt_2Ga, PtGa, and $PtGa_2$ have been successfully grown on GaAs by MBE. The results of annealing studies are in good agreement with the Pt-Ga-As ternary phase diagram. $PtGa_2$ and PtGa films are chemically stable on GaAs up to 450°C and 600°C, respectively. However, the Pt_2Ga films start

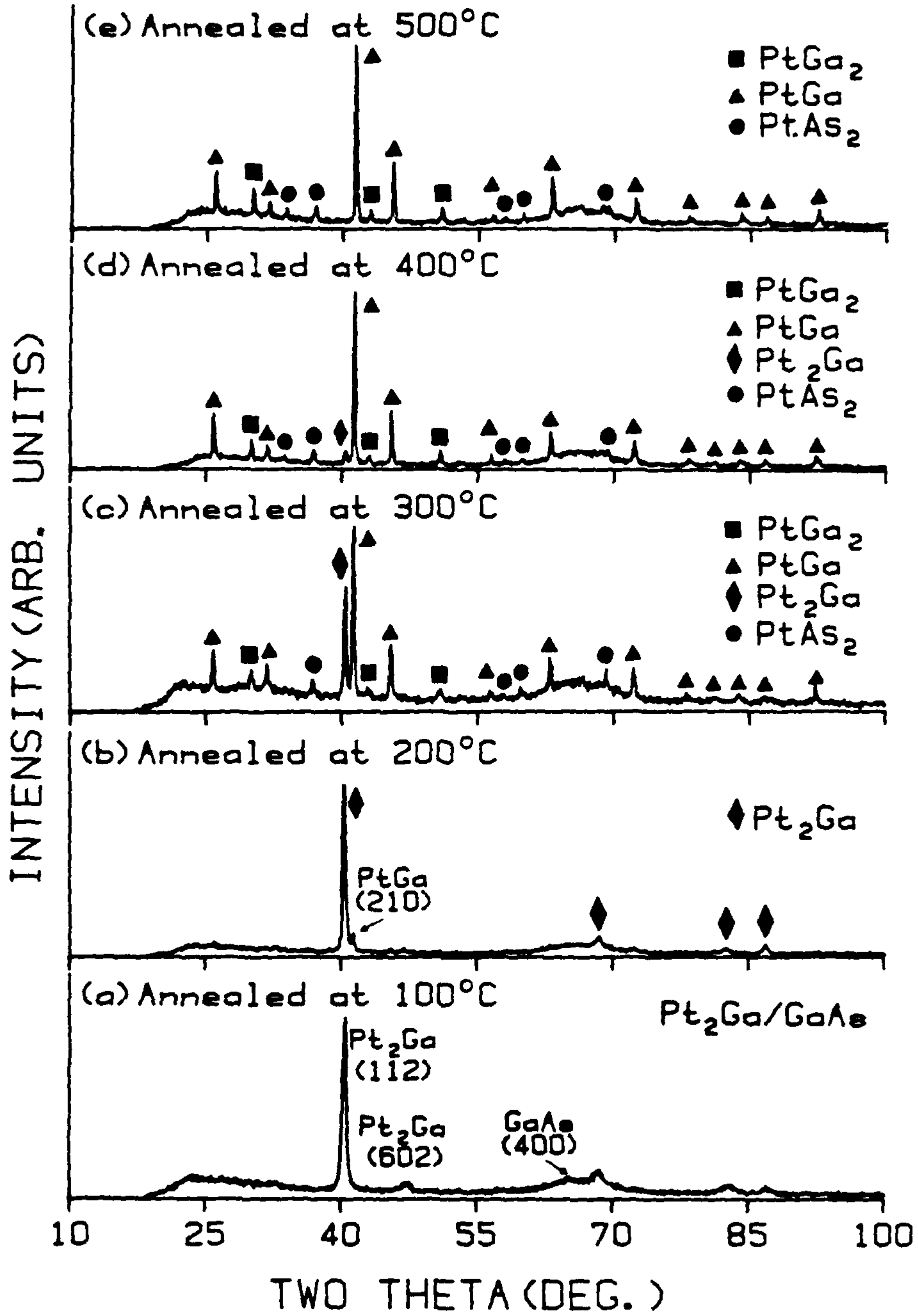

Fig. 3. XRD patterns of Pt_2Ga thin films on GaAs(100) for sample annealed to (a) 100°C, (b) 200°C, (c) 300°C, (d) 400°C and (e) 500°C.

to react with GaAs even at temperatures of 200°C to produce PtGa, $PtGa_2$, Pt_3Ga_7 and $PtAs_2$ at temperatures of 500°C. It has been shown here that the thermodynamics of bulk materials can be used to control the chemistry at the metal/semiconductor interface. In order to understand the Pt-Ga intermetallic system further, several additional studies including annealing studies under As ambient, temperature dependent TEM and transport measuremeants of various intermetallic Pt-Ga phases grown by MBE still need to be carried out.

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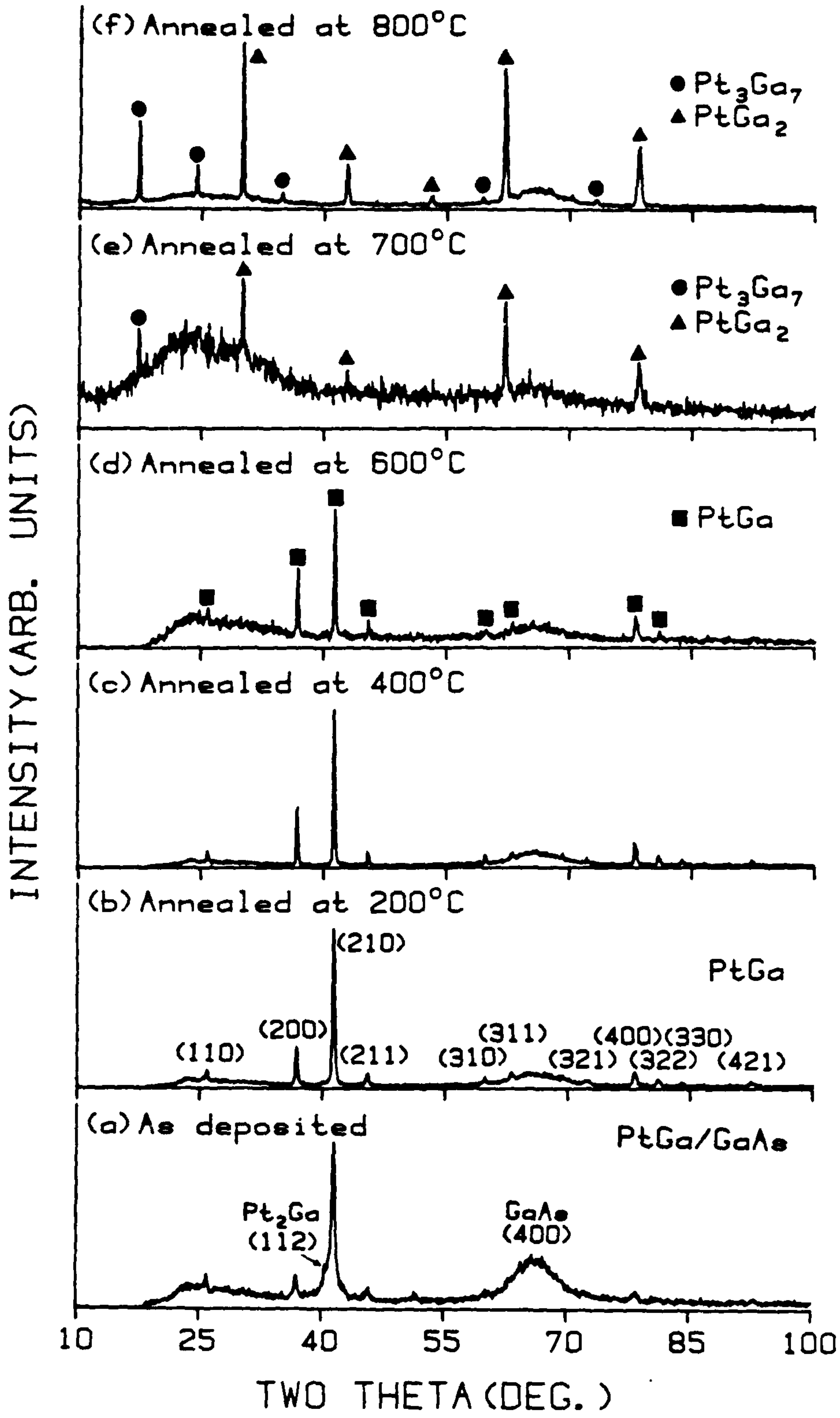

Fig. 4. XRD patterns of PtGa thin films on GaAs (100) for (a) the as-deposited film and after the sample was annealed to (b) 200°C, (c) 400°C, (d) 600°C, (e) 700°C and (f) 800°C.

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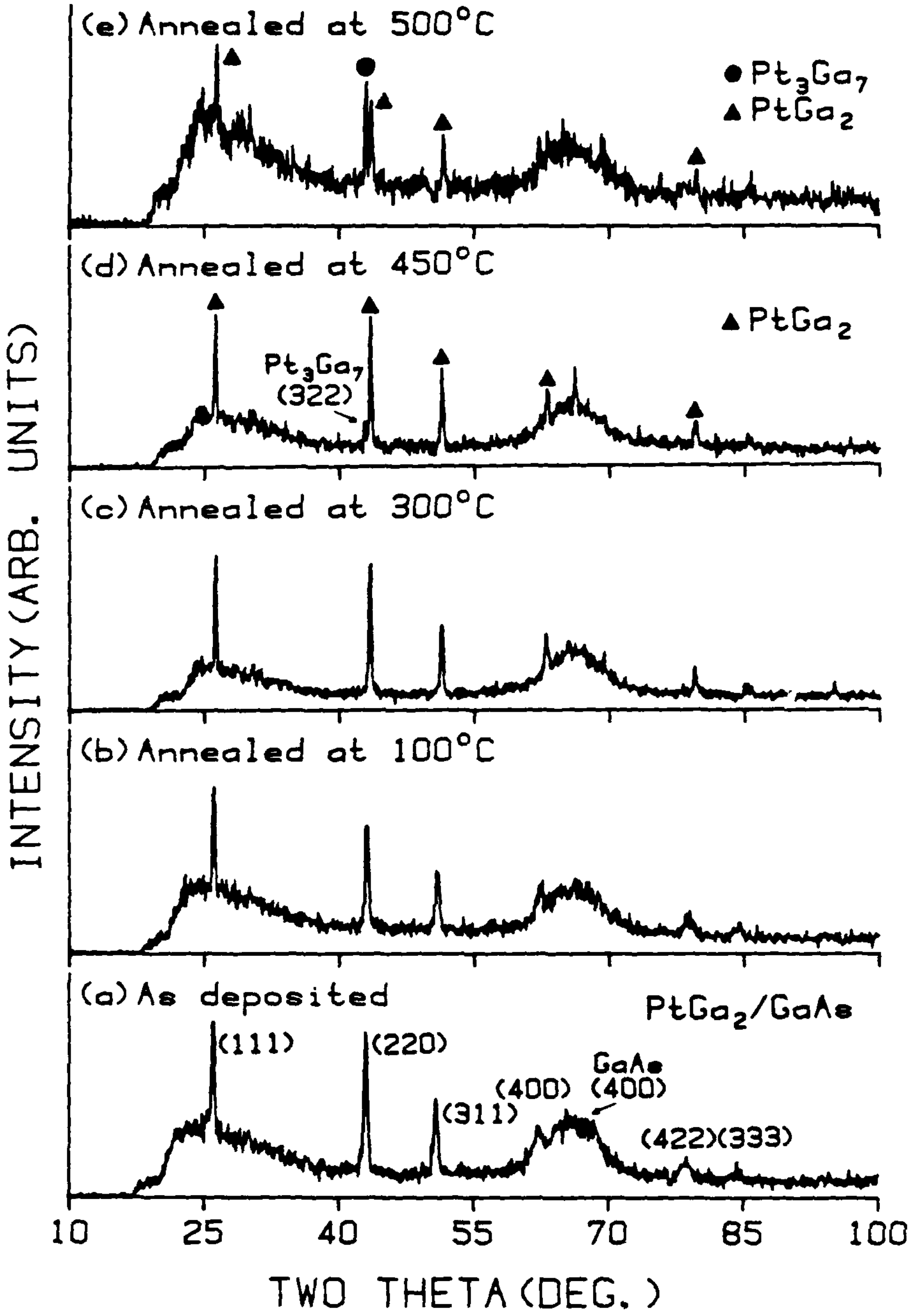

Fig. 5. XRD patterns of $PtGa_2$ thin films on GaAs (100) for (a) the as-deposited film and after the sample was annealed to (b) 100°C, (c) 300°C, (d) 450°C and (e) 500°C.

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