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Research Contract N00014-87-K-0014
R&T Code 413a001

Technical Report No. 16

THERMODYNAMICALLY STABLE CONDUCTING FILMS
OF INTERMETALLIC PtGa₂ ON GALLIUM ARSENIDE

by

Larry P. Sadwick,* Kang L. Wang,*
David K. Shuh,[†] Young K. Kim,[†] and R. Stanley Williams[†]

To be published

in

Proc. Mat. Res. Soc. Spring Symp. in San Diego, 1989

University of California, Los Angeles

[†]Department of Chemistry & Biochemistry and Solid State Science Center
Los Angeles, CA 90024-1569

and

*Department of Chemical Engineering
Los Angeles, CA 90024-1594

July 1, 1989

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AD-A210 077

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REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b RESTRICTIVE MARKINGS N/A		
2a SECURITY CLASSIFICATION AUTHORITY N/A			3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release; distribution unlimited		
2b DECLASSIFICATION / DOWNGRADING SCHEDULE N/A					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) N/A			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION The Regents of the University of California		6b OFFICE SYMBOL (if applicable)	7a NAME OF MONITORING ORGANIZATION 1) ONR Pasadena - Administrative 2) ONR Alexandria - Technical		
6c ADDRESS (City, State, and ZIP Code) Office of Contracts & Grants Administration U C L A, 405 Hilgard Avenue Los Angeles, CA 90024			7b ADDRESS (City, State, and ZIP Code) 1) 1030 E. Green Street, Pasadena, CA 91106 2) 800 N. Quincy St., Arlington, VA 22217-5000		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research		8b OFFICE SYMBOL (if applicable) ONR	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-87-K-0014		
8c ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street, 614A:DHP Arlington, VA 22217-5000			10 SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
					WORK UNIT ACCESSION NO.
11 TITLE (Include Security Classification) UNCLASSIFIED: Thermodynamically stable conducting films of intermetallic PtGa ₂ on gallium arsenide					
12 PERSONAL AUTHOR(S) Larry P. Sadwick, Kang L. Wang, David K. Shuh, Young K. Kim and R. Stanley Williams					
13a TYPE OF REPORT Tech. Rept. #16		13b TIME COVERED FROM 1988 TO 1989		14 DATE OF REPORT (Year, Month, Day) 20 June 1989	15 PAGE COUNT 6
16 SUPPLEMENTARY NOTATION					
17. COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	epitaxial films - ultra-high vacuum - chemical stability - compound semiconductors - contact degradation - Schottky barrier - Fermi level pinning. (STES) ←		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) The first epitaxial platinum gallium two (PtGa ₂) films have been grown on gallium arsenide (GaAs)(100) by co-evaporation of the elements under ultra-high vacuum conditions. An electron-beam evaporator and a Knudsen cell were used to produce the platinum and gallium beams, respectively. The resulting films and bulk PtGa ₂ have been characterized by x-ray diffraction, Auger electron spectroscopy, and x-ray photoelectron spectroscopy. The data confirm the PtGa ₂ stoichiometry and crystal structure of the films, and demonstrate their chemical stability on GaAs(100). This study supports the contention that PtGa ₂ can be a suitable, temperature-stable contact material on GaAs substrates.					
20 DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED		
22a NAME OF RESPONSIBLE INDIVIDUAL R. Stanley Williams			22b TELEPHONE (Include Area Code) (213) 825-8818		22c OFFICE SYMBOL UCLA

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Larry P. Sadwick*, Kang L. Wang*, David K. Shuh**, Young K. Kim**, and R. Stanley Williams**

*University of California Los Angeles Department of Electrical Engineering Device Research Laboratory, 7732 Boelter Hall, Los Angeles, CA 90024

**University of California Los Angeles Department of Chemistry and Biochemistry and Solid Science Center, 2080 Young Hall, Los Angeles, CA 90024.

ABSTRACT

The first epitaxial platinum gallium two (PtGa₂) films have been grown on gallium arsenide (GaAs) (100) by co-evaporation of the elements under ultra-high vacuum conditions. An electron beam evaporator and a Knudsen cell were used to produce the platinum and gallium beams, respectively. The resulting films and bulk PtGa₂ have been characterized by x-ray diffraction, Auger electron spectroscopy, and x-ray photoelectron spectroscopy. The data confirm the PtGa₂ stoichiometry and crystal structure of the films, and demonstrate their chemical stability on GaAs (100). This study supports the contention that PtGa₂ can be a suitable, temperature stable contact material on GaAs substrates.

Introduction

The chemistry of metal-semiconductor interfaces ultimately controls the nature of Schottky barrier or Ohmic contact formation [1]. Contact formation on elemental semiconductors is relatively straightforward because of the simplicity of binary phase systems, which have a limited number of reaction products. Transition to compound semiconductor technology has encountered additional difficulty because ternary phase diagrams are significantly more complex and rarely well characterized [2].

In order to employ GaAs based electronic devices for both high reliability and harsh environment applications, chemically stable contacts must be formed at the metal-semiconductor interface. Conventional methods to alleviate temperature induced contact degradation usually involve passivation or interdiffusion barriers [3].

A simple solution to the degradation problem would be the use of an intermetallic compound that is thermodynamically stable to the GaAs surface and that also possesses suitable electronic transport properties [4]. Therefore, the intention of this study was to select and investigate an intermetallic contact on GaAs system chosen from a known ternary phase diagram. The intermetallic compound should exhibit a thermodynamically stable tie-line to the GaAs semiconductor. A further consideration is that the intermetallic should be compatible with existing molecular beam epitaxy (MBE) techniques.

On the basis of the Pt-Ga-As ternary phase diagram, as experimentally elucidated by Tsai et. al. [5] and illustrated in Fig. 1, PtGa₂ was selected as a candidate for thin film growth on GaAs (100). The existence of the pseudobinary tie-line between PtGa₂ and GaAs implies that the two bulk compounds do not react with each other in a closed system. PtGa₂ is a thermodynamically favored reaction product of the Pt-Ga-As system. Depositing an elemental Pt film on GaAs and then annealing will induce chemical reactions that yield intermetallic compounds of Pt with both Ga and As, accompanied by the subsequent degradation of the interface [5]. Since

PtGa₂ is a potential product of such a reaction, it will be much more stable in contact with GaAs than Pt.

Advanced device considerations require that the contacts on GaAs be stable to temperatures in excess of 800°C. The PtGa₂ films are stable up to 450°C in air during long-time anneals; further work involving capping or other equivalent procedures is required to determine if stability above 800°C can be achieved.

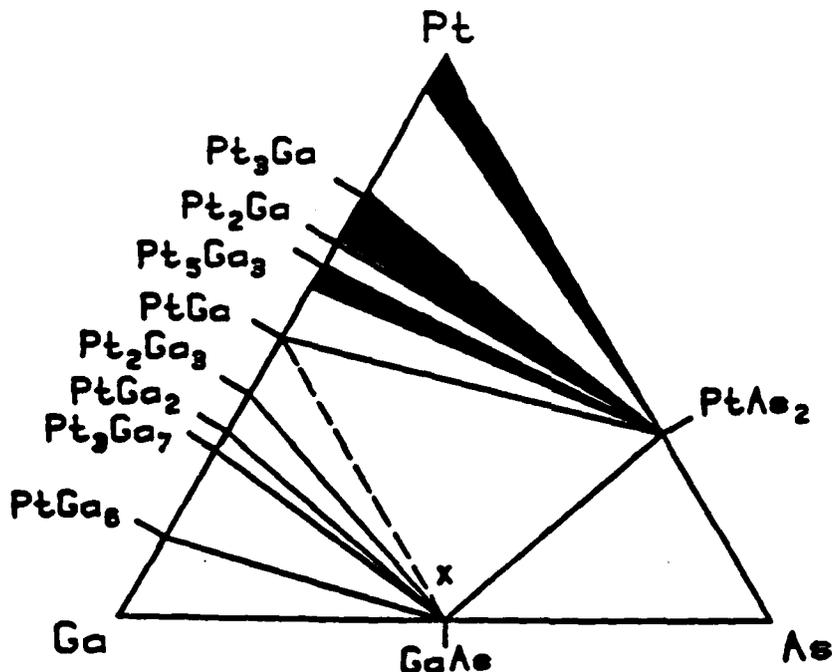


Figure 1. Solidus portion of Pt-Ga-As ternary phase diagram at 25 ° C.

Growth

The PtGa₂ films were grown in a MBE chamber with a base pressure of 2×10^{-10} torr and a deposition pressure of 4×10^{-9} torr. The two inch GaAs wafers were introduced via a cryopumped load lock system and mounted on a modified manipulator equipped with radiative heating elements. The samples were cleaned by heating to a temperature of 550°C under an arsenic overpressure obtained from a Knudsen cell to prevent surface decomposition of the GaAs. 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 tantalum heating element. The fluxes of platinum and gallium were initially tuned to the proper stoichiometry. PtGa₂ can be visually identified by its characteristic golden color, as PtGa₂ is the only Pt-Ga phase that has a band structure similar to that of elemental gold [5,6]. 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 PtGa₂ films, the flux ratio of gallium to platinum was adjusted to slightly greater than 2 to 1. Co-evaporation of the PtGa₂ proceeded with the sample held at substrate temperatures ranging from near room temperature to over 500°C at an epilayer growth of approximately 5 microns/hour.



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Structural and Chemical Characterization

Powder x-ray diffractometry (XRD) patterns of the films were taken on a Philips diffractometer utilizing a Crystal Logic interface to a DEC VAX 11/750 mainframe computer. Diffraction patterns were obtained by accumulation of data for periods of time upwards of twelve hours to achieve an adequate signal to noise ratio. The thin PtGa₂ films were annealed in a tube furnace under both nitrogen and air ambients. The film composition and crystallite orientation was subsequently determined by XRD to ascertain the temperature behavior of the epitaxially deposited material. Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) of the PtGa₂ thin films and bulk material were performed in a KRATOS XSAM 800 spectrometer that was equipped with a sample treatment chamber (STC), scanning electron microscope (SEM) and ES300 electron spectrometer. In addition, the sample analysis chamber was equipped with a manipulator capable of heating samples up to 450°C while in the analysis position. The base pressure during sample analysis was 2×10^{-10} torr. The samples were subjected to short, low current, rastered 3 KeV ion bombardments until AES revealed no carbon or oxygen contaminants. The samples were then annealed at various temperatures (maximum 450°C) after which AES and XPS data were collected. The XPS data were collected using an aluminum K α excitation source.

Results and Discussion

The resultant films were specular under both optical and SEM examination and golden in appearance. The films were determined to be PtGa₂ by the analytical techniques described above. The range of composition of PtGa₂ is very narrow, unlike many other intermetallic compounds which have a wide acceptance range of compositions. Figure 2a shows a powder XRD pattern of an oriented PtGa₂ (110) film (as seen by the 220 reflection at 43.3°) which was grown on a GaAs (100) substrate at room temperature. Figure 2b shows the XRD pattern obtained after the sample had been annealed at 200°C in a conventional furnace tube. The PtGa₂ peaks are virtually unchanged after subsequent annealing to 400°C as shown in figure 2c. The XRD patterns of figures 2a through c consists of peaks solely due to PtGa₂ and GaAs. The peaks at 26.0°, 43.3° and 51.0° are the (111), (220) and (311) reflections of PtGa₂, respectively. The peak at 66° is the (400) reflection from the (100) GaAs substrate. The XRD pattern showed no observable change from room temperature to annealing temperatures on the order of 450°C. Above 450°C, a small peak around 42.5° was detected. This peak is most probably due to the formation of a Pt₃Ga₇ phase which coexists with the PtGa₂ phase. At temperatures above 550°C, a sharp decrease in the intensity of the PtGa₂ peaks occurred in conjunction with the appearance of peaks due to PtGa and, most likely, PtAs₂.

The electron spectroscopies clearly indicate that the thin film samples have the same stoichiometry and valence band structure as that of a bulk PtGa₂ sample. This further served as a verification of the identity and uniformity of the thin PtGa₂ films. The stoichiometries were determined by comparisons of the relative peak to peak response of the AES and by the relative peak areas of the XPS data between the thin film samples and a bulk standard. Figure 3 shows the AES signals from a thin film of PtGa₂ on GaAs. The electron distribution curves (EDC) determined from the core levels and valence bands are presented in Figs. 4 and 5. In all cases, the thin films produced results that were indistinguishable from the bulk sample.

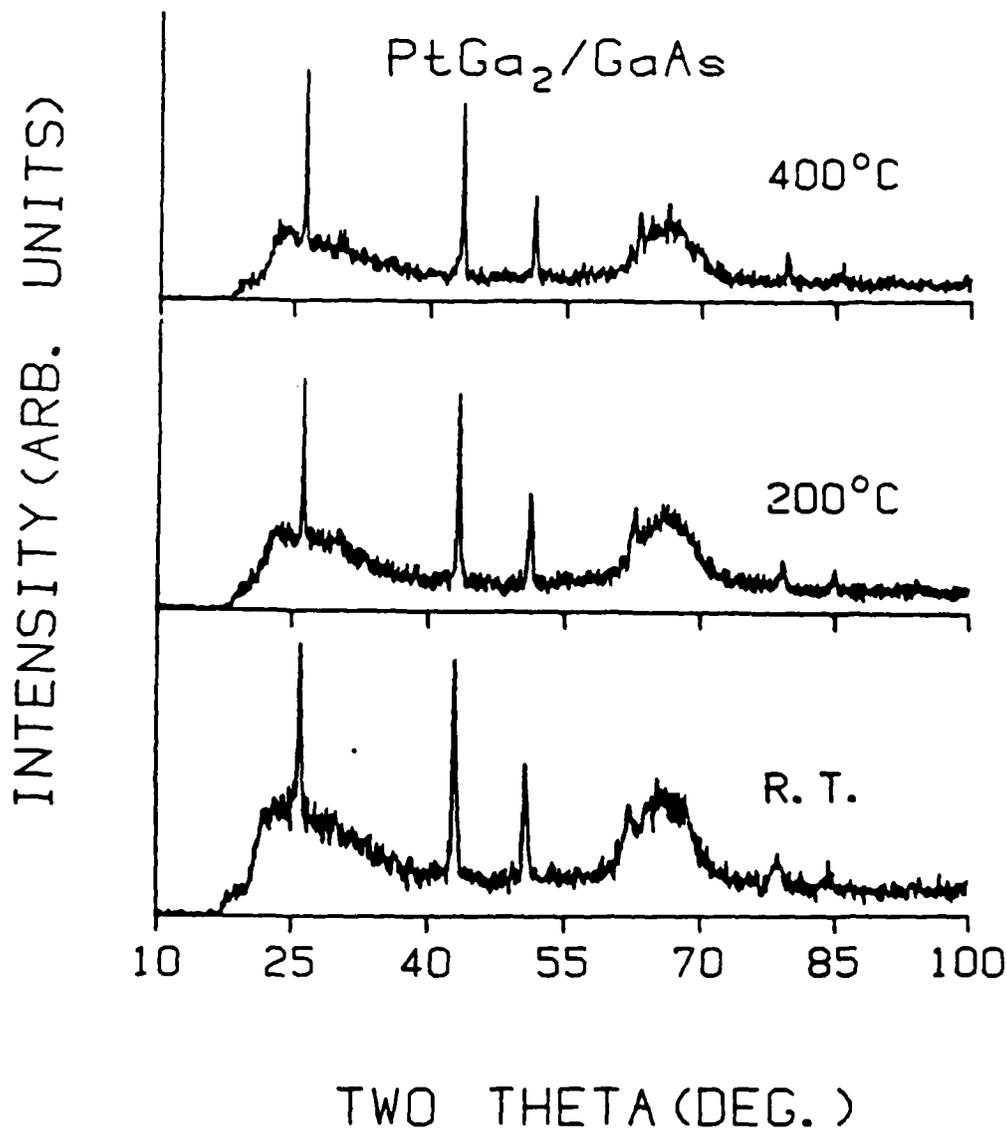


Figure 2. XRD pattern of PtGa₂ on (100) GaAs. 2a: room temperature, 2b: annealed at 200°C, 2c: annealed at 400°C. All peaks except the (400) GaAs at 66° correspond to PtGa₂.

Conclusions

The successful growth on GaAs (100) of an intentionally designed stable intermetallic thin film that is similar to silicides currently employed in standard silicon processing has been demonstrated. The PtGa₂ films are chemically stable on GaAs (100) up to 450°C. PtGa₂ shows promise as a suitable contacting material for high reliability applications.

The formation of thermochemically stable PtGa₂ epilayers on GaAs will provide an interesting system for the investigation into the nature of Schottky barrier formation and subsequent Fermi level pinning at the interface. We believe that chemically stable PtGa₂ intermetallics should eliminate many of the possible chemical factors which influence or effect the phenomenon of Fermi level pinning.

Work in progress to further understand the PtGa family-GaAs system includes temperature-dependent TEM, transport measurements and the characterization of various intermediate Pt-Ga phases grown by MBE [7].

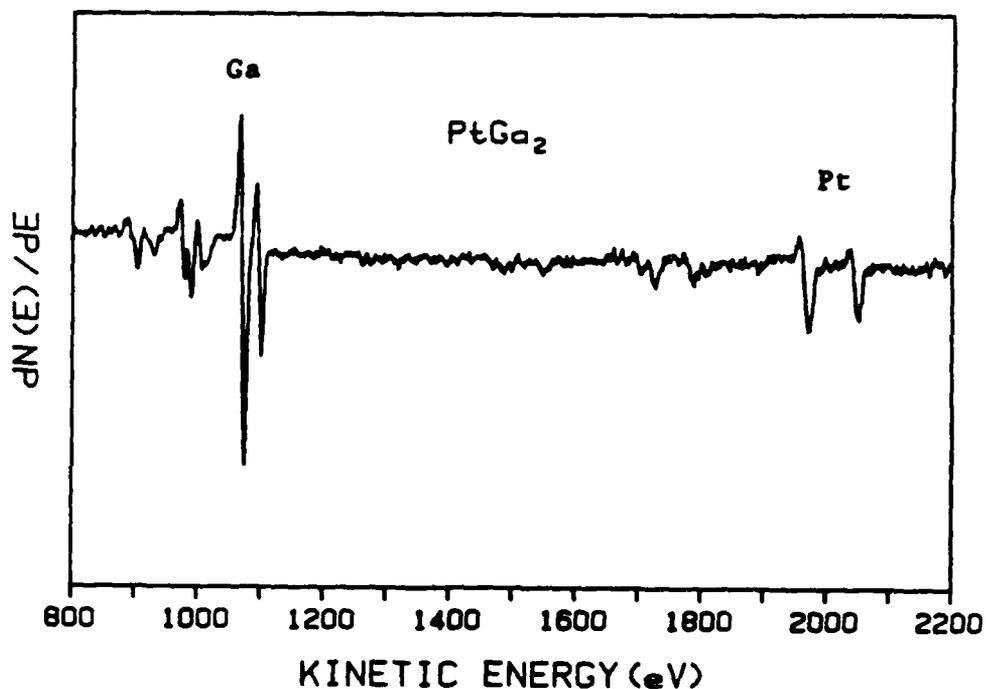


Figure 3. AES spectra of PtGa₂ film. The only observable peaks are due to Ga and Pt. The calculated ratio is Ga:Pt 2:1.

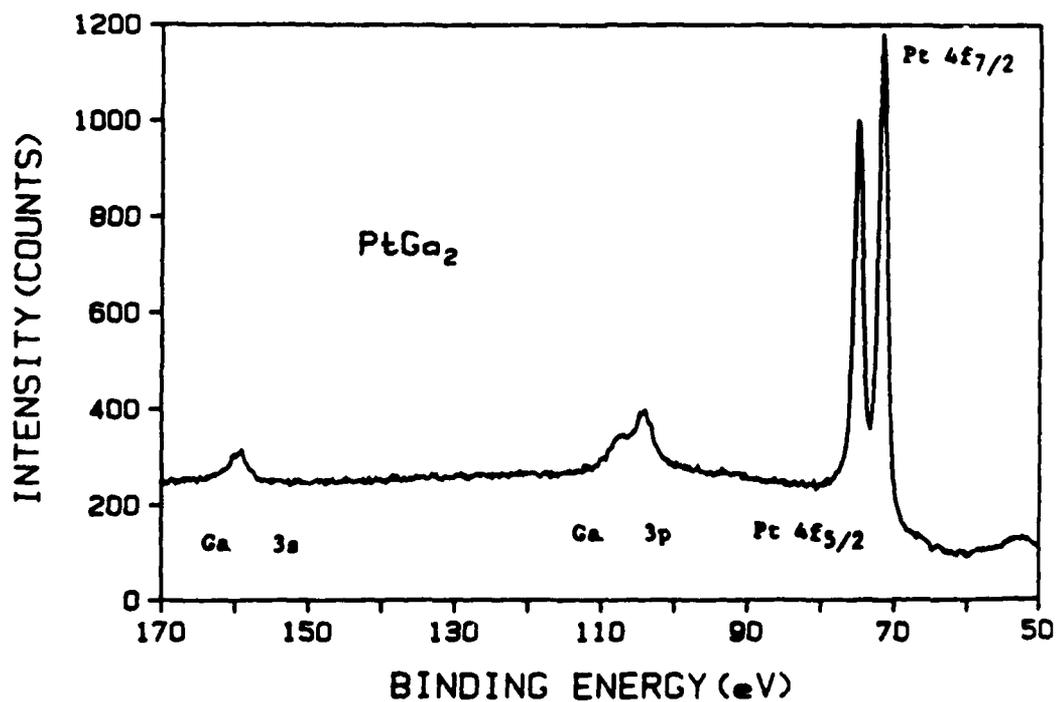


Figure 4. XPS binding energy spectra of PtGa₂ film.

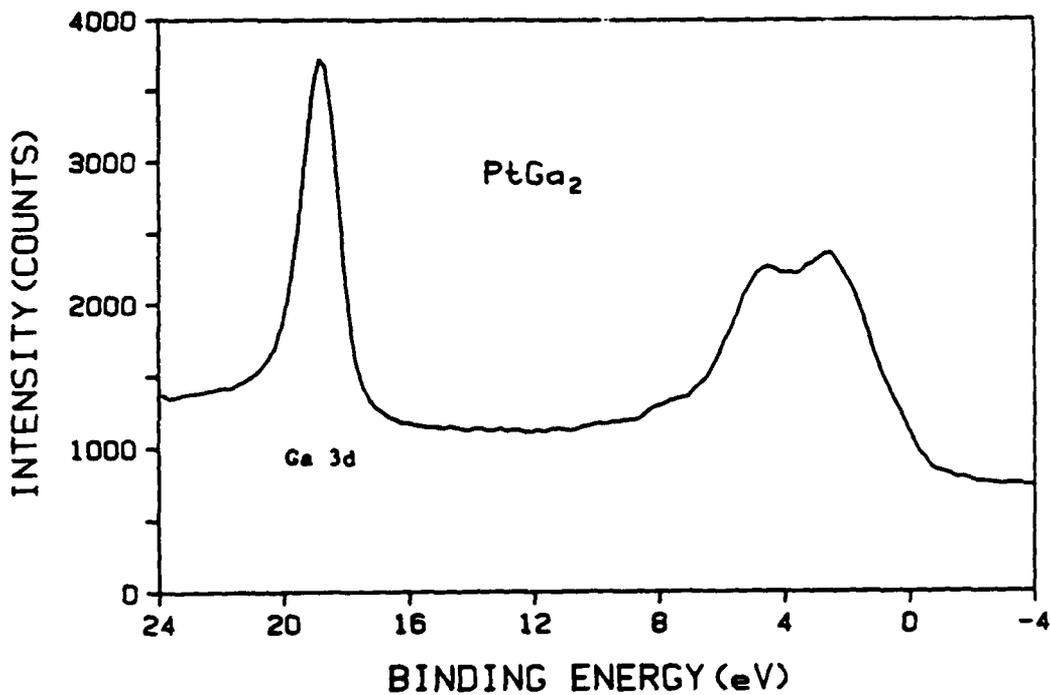


Figure 5. Valance band of PtGa₂ film which is identical to bulk PtGa₂.

Acknowledgements

This work was supported by the office of Naval Research/SDIO, the State of California MICRO program and Hughes Aircraft. RSW received further support from the Alfred P. Sloan and the Camille and Henry Dreyfuss Foundations.

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- Dr. J. Buehler
Chemistry & Chem. Engrg.
Cals. Inst. of Technology
Pasadena, CA 91125
- Dr. Paul G. Barbara
Department of Chemistry
University of Minnesota
Minneapolis, MN 55455-0431
- Dr. Duncan W. Brown
Adv. Technology Matls., Inc.
520-B Deabury Road
New Milford, CT 06776
- Dr. S. Brackenstein
Department of Chemistry
State University of NY
Buffalo, NY 14214
- Dr. J. Beiler
Naval Research Laboratory
Code 6115
Washington, DC 20375-5000
- Dr. R.P.H. Chang
Matls. Science & Engineering
Northwestern University
Evanston, IL 60208
- Dr. Paul A. Christian
Adv. Chem. Technol., Fed. Systems
Eastman Kodak Company
Rochester, NY 14650-2156
- Dr. Richard Colton
Code 6170
Naval Research Laboratory
Washington, DC 20375-5000
- Dr. J.E. Demuth
IBM Watson Research Center
PO Box 218
Yorktown Heights, NY 10598
- Dr. F.J. DiSalvo
Department of Chemistry
Cornell University
Ithaca, NY 14853
- Dr. A.B. Ellis
Department of Chemistry
University of Wisconsin
Madison, WI 53706
- Dr. M.A. El-Sayed
Chemistry Department
University of California
Los Angeles, 90024-1569
- Dr. John Eyster
Department of Chemistry
University of Florida
Gainesville, FL 32611
- Dr. James F. Garvey
Department of Chemistry
State University of New York
Buffalo, NY 14214
- Dr. T.F. George
Chemistry/Physics Depts.
State University of New York
Buffalo, NY 14260
- Dr. Arold Green
Quantum Surface Dynamics Br.
Naval Weapons Ctr. Code 3817
China Lake, CA 93555
- Dr. R. Hamers
IBM Watson Research Center
PO Box 218
Yorktown Heights, NY 10598
- Dr. Paul K. Hansma
Department of Physics
University of California
Santa Barbara, CA 93106
- Dr. C.B. Harris
Chemistry Dept.
University of California
Berkeley, CA 94720
- Dr. J.C. Hemminger
Chemistry Dept.
University of California
Irvine, CA 92717
- Dr. Roald Hoffmann
Chemistry Dept.
Cornell University
Ithaca, NY 14853
- Dr. L. Inerente
Chemistry Dept.
Rensselaer Polytech. Inst.
Troy, NY 12181
- Dr. E.A. Irene
Chemistry Dept.
Univ. of North Carolina
Chapel Hill, NC 27514
- Dr. D.E. Irish
Department of Chemistry
University of Waterloo
ONT N2L 3G1, Canada
- Dr. R.E. Smailley
Department of Chemistry
Rice University, Box 1892
Houston, TX 77251
- Dr. G.A. Somorjai
Chemistry Dept.
University of California
Berkeley, CA 94720
- Dr. Sylvia M. Johnson
SRJ International
333 Ravenswood Avenue
Menlo Park, CA 94025
- Dr. Z.H. Kafafi
Optical Sci. Div. Code 6551
Naval Research Laboratory
Washington, DC 20375-5000
- Dr. George H. Morrison
Chemistry Dept.
Cornell University
Ithaca, NY 14853
- Dr. Daniel M. Neumark
Chemistry Department
University of California
Berkeley, CA 94720
- Dr. D. Ramaker
Chemistry Dept.
George Washington Univ.
Washington, DC 20052
- Dr. R. Reeves
Chemistry Dept.
Rensselaer Polytech. Inst.
Troy, NY 12181
- Dr. A. Reisman
Microelectronics Center
Research Triangle Park
No. Carolina, 27709
- Dr. G. Ruboff
IBM Watson Research Ctr.
PO Box 218
Yorktown Hgts, NY 10598
- Dr. Richard J. Saylor
Chemistry Department
University of California
Berkeley, CA 94720
- Dr. Robert W. Shaw
US Army Research Office
Box 12211
Res. Triangle Park, NC 27709
- Dr. S. Sibener
James Franck Institute
University of Chicago
Chicago, IL 60637
- Dr. N. Winograd
Chemistry Dept.
Case Western Res. Univ.
University Park, PA 16802
- Dr. A. Wold
Chemistry Dept.
Brown University
Providence, RI 02912
- Dr. John T. Yates
Chemistry Dept.
University of Pittsburgh
Pittsburgh, PA 15260
- Dr. E. Yeager
Chemistry Dept.
Case Western Reserve Univ.
Cleveland, OH 41106
- Dr. R.E. Smalley
Department of Chemistry
Rice University, Box 1892
Houston, TX 77251
- Dr. G.A. Somorjai
Chemistry Dept.
University of California
Berkeley, CA 94720
- Dr. Sylvia M. Johnson
SRJ International
333 Ravenswood Avenue
Menlo Park, CA 94025
- Dr. Z.H. Kafafi
Optical Sci. Div. Code 6551
Naval Research Laboratory
Washington, DC 20375-5000
- Dr. George H. Morrison
Chemistry Dept.
Cornell University
Ithaca, NY 14853
- Dr. Daniel M. Neumark
Chemistry Department
University of California
Berkeley, CA 94720
- Dr. D. Ramaker
Chemistry Dept.
George Washington Univ.
Washington, DC 20052
- Dr. R. Reeves
Chemistry Dept.
Rensselaer Polytech. Inst.
Troy, NY 12181
- Dr. A. Reisman
Microelectronics Center
Research Triangle Park
No. Carolina, 27709
- Dr. G. Ruboff
IBM Watson Research Ctr.
PO Box 218
Yorktown Hgts, NY 10598
- Dr. Richard J. Saylor
Chemistry Department
University of California
Berkeley, CA 94720
- Dr. Robert W. Shaw
US Army Research Office
Box 12211
Res. Triangle Park, NC 27709
- Dr. S. Sibener
James Franck Institute
University of Chicago
Chicago, IL 60637
- Dr. N. Winograd
Chemistry Dept.
Case Western Res. Univ.
University Park, PA 16802
- Dr. A. Wold
Chemistry Dept.
Brown University
Providence, RI 02912
- Dr. John T. Yates
Chemistry Dept.
University of Pittsburgh
Pittsburgh, PA 15260
- Dr. E. Yeager
Chemistry Dept.
Case Western Reserve Univ.
Cleveland, OH 41106
- Dr. R.E. Smalley
Department of Chemistry
Rice University, Box 1892
Houston, TX 77251
- Dr. G.A. Somorjai
Chemistry Dept.
University of California
Berkeley, CA 94720
- Dr. Sylvia M. Johnson
SRJ International
333 Ravenswood Avenue
Menlo Park, CA 94025
- Dr. Z.H. Kafafi
Optical Sci. Div. Code 6551
Naval Research Laboratory
Washington, DC 20375-5000
- Dr. George H. Morrison
Chemistry Dept.
Cornell University
Ithaca, NY 14853
- Dr. Daniel M. Neumark
Chemistry Department
University of California
Berkeley, CA 94720
- Dr. D. Ramaker
Chemistry Dept.
George Washington Univ.
Washington, DC 20052
- Dr. R. Reeves
Chemistry Dept.
Rensselaer Polytech. Inst.
Troy, NY 12181
- Dr. A. Reisman
Microelectronics Center
Research Triangle Park
No. Carolina, 27709
- Dr. G. Ruboff
IBM Watson Research Ctr.
PO Box 218
Yorktown Hgts, NY 10598
- Dr. Richard J. Saylor
Chemistry Department
University of California
Berkeley, CA 94720
- Dr. Robert W. Shaw
US Army Research Office
Box 12211
Res. Triangle Park, NC 27709
- Dr. S. Sibener
James Franck Institute
University of Chicago
Chicago, IL 60637
- Office of Naval Research
Chemistry Div., Code 1113
800 N. Quincey Avenue
Arlington, VA 22217-5000
- Chief of Naval Research
Spec. Assistant, Marine Corps
Code 00MC
800 N. Quincey Street
Arlington, VA 22217-5000
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Naval Weapons Support Center
Attn: Dr. Bernard E. Douda
Oran, IN 47522-5050
- Dr. Richard W. Drisko
Naval Civil Engineering Lab
Code L-52
Port Huene, CA 93043
- Defense Tech. Information Ctr.
Building 5
Cameron Station
Alexandria, VA 22314
- David Taylor Research Center
Attn: Dr. Eugene C. Fischer
Applied Chemistry Division
Annapolis, MD 21402-5067
- Dr. James S. Murlay
Chemistry Div., Code 6100
Naval Research Laboratory
Washington, DC 20375-5000
- Dr. David Nelson
Office of Naval Res. Code 413
800 N. Quincey Street
Arlington, VA 22217-5000
- Dr. Ronald L. Aikins
Chemistry Div., Code 385
Naval Weapons Center
China Lake, CA 93555-6001
- Dr. Bernadette Eichinger
Naval Ships Systems Engr. Station
Phila. Naval Base, Code 053
Philadelphia, PA 19112
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Attn: Dr. H. H. Singerman
Code 283
Annapolis, MD 21402-5067
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Naval Ocean Systems Center
Code 52
San Diego, CA 91232
- Carlota Leafroy
Office of Naval Research
1030 E. Green Street
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