

A comparison by means of calorimetry of solid state interdiffusion reactions in Ni/Zr and Ni/Ti composites

B. E. White Jr., M. E. Patt, and E. J. Cottis

Citation: [Journal of Applied Physics](#) **68**, 1910 (1990); doi: 10.1063/1.346581

View online: <http://dx.doi.org/10.1063/1.346581>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jap/68/4?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Maximum thickness of amorphous NiZr interlayers formed by a solid-state reaction technique](#)

Appl. Phys. Lett. **51**, 1693 (1987); 10.1063/1.98546

[Solid-state interdiffusion reactions in Ni/Ti and Ni/Zr multilayered thin films](#)

Appl. Phys. Lett. **51**, 661 (1987); 10.1063/1.98326

[Differential scanning calorimetry study of solid-state amorphization in multilayer thin-film Ni/Zr](#)

Appl. Phys. Lett. **50**, 566 (1987); 10.1063/1.98136

[Transmission electron microscopic observations of amorphous NiZr alloy formation by solid-state reaction](#)

Appl. Phys. Lett. **48**, 1436 (1986); 10.1063/1.96881

[Dominant moving species in the formation of amorphous NiZr by solid-state reaction](#)

Appl. Phys. Lett. **47**, 800 (1985); 10.1063/1.95988



Powerful, Multi-functional UV-Vis-NIR and FTIR Spectrophotometers

Providing the utmost in sensitivity, accuracy and resolution for applications in materials characterization and nano research

- Photovoltaics
- Polymers
- Thin films
- Paints
- Ceramics
- DNA film structures
- Coatings
- Packaging materials

[Click here to learn more](#)



A comparison by means of calorimetry of solid state interdiffusion reactions in Ni/Zr and Ni/Ti composites

B. E. White, Jr., M. E. Patt, and E. J. Cottis

Department of Physics, Applied Physics and Astronomy, State University of New York at Binghamton, Binghamton, New York 13901

(Received 22 September 1989; accepted for publication 26 April 1990)

We have investigated solid state amorphization reactions in mechanically deformed composites in both the Ni-Ti system and the Ni-Zr system. The growth of amorphous material in our Ni/Ti composites is apparently facilitated by the relatively large degree of disorder induced in the metal layers by the mechanical deformation process. The growth of amorphous material is slower in Ni/Ti composites than in Ni/Zr composites, while we found similar kinetic constraints on the formation of equilibrium compounds in both systems. Thus the maximum thickness of amorphous Ni-Ti layers was an order of magnitude less than the 1000-Å layers grown in the Ni-Zr system.

Single phase amorphous alloys can form in diffusion couples at relatively low temperatures (approximately half pertinent melting temperatures) by means of interdiffusion of pure, polycrystalline elements.¹⁻¹² The present study concerns a comparison of solid state reactions in the Ni-Ti system and the Ni-Zr system. As both Zr and Ti are IVB elements, these systems are considered to be chemically and thermodynamically similar.¹³⁻¹⁸ But while amorphous material has been observed to grow to a thickness of up to 1000 Å at Ni/Zr interfaces,^{2,10-12,19-24} such prodigious growth has not been observed in the Ni/Ti composites.^{13,21,23,25} In fact, some investigators have observed the growth only of equilibrium intermetallic compounds in Ni/Ti diffusion couples,¹³ while in a different investigation the growth of amorphous material in Ni/Ti diffusion couples was observed only when a sufficient degree of disorder was initially present at the Ni/Ti interfaces.²¹⁻²³ No such contrast is apparent in the production of amorphous alloys in these systems by means of ball milling powders, where amorphous alloys are routinely produced in both the Ni-Zr and the Ni-Ti systems.²⁶⁻²⁹

In the present work we sought to investigate the difference in the reaction kinetics in these two systems by means of differential scanning calorimetry (DSC) measurements³⁰ on mechanically deformed,³¹ multilayered composites of Ni/Zr and Ni/Ti. Samples utilized for study are composites of similar average stoichiometries (near equiatomic), prepared by means of mechanical codeformation of polycrystalline foils enclosed in stainless-steel sheaths. The composites were observed to deform in the rolling mill in nearly identical fashion and scanning electron microscopy revealed similar layer thicknesses in both systems. The structures and phases of the samples in the as-prepared state as well as at various degrees of reaction are characterized by means of x-ray diffraction analysis and transmission electron microscopy. Reactions in diffusion couples of the Ni-Ti system or the Ni-Zr system are initiated as the samples (hermetically sealed in aluminum pans) are heated at a constant rate above room temperature in the DSC. The rate of heat release is measured by means of DSC through the course of a reaction.

Each DSC scan was followed by a second scan (identical thermal conditions) of the same sample; the data from the second scan were subtracted from the data of the first scan.

A comparison of solid state reactions by means of DSC (Fig. 1) indicates that at lower temperatures the solid state reaction in the Ni/Zr composite is significantly faster than the solid state reaction in the Ni/Ti composite. Upon heating a Ni/Ti diffusion couple from 300 to 850 K at 20 K/min in a differential scanning calorimeter (Fig. 1) a significant rate of heat release is first observed at about 580 K. This is in contrast to the reaction rate observed in the Ni/Zr diffusion couple of similar geometry, where upon being heated to a temperature of 580 K the solid state reaction has already consumed a significant amount of the sample. The DSC scan of the Ni/Ti composite indicates that above a temperature of 580 K the reaction rate increases monotonically until a temperature of approximately 660 K. At this temperature a distinct peak is observed in the DSC scan followed by a marked decrease in the reaction rate and a series of DSC peaks. X-ray analysis (Fig. 2) of similar samples heated to temperatures of 660 K and rapidly cooled to room temperature reveal Bragg peaks corresponding to the elements Ni and Ti, and a broad peak centered at $2\theta \approx 43.5^\circ$. Such a broad peak in x-ray scans is indicative of amorphous material,^{18,25} and the angle of its maximum corresponds to that of liquid-quenched metallic glass of composition near $\text{Ni}_{63}\text{Ti}_{37}$. X-ray analysis [Fig. 2(c)] of similar samples heated to temperatures of 670 K and rapidly cooled to room temperature reveal a new Bragg peak corresponding to the intermetallic compound $\text{Ni}_{50}\text{Ti}_{50}$ with a CsCl structure, indicating that a small amount of crystalline material has been formed.^{32,33} Upon examining numerous such Ni/Ti composites utilizing DSC and x-ray analysis we are able to correlate such a distinct change in the kinetics of the solid state reaction (as evidenced by a peak at a temperature near 670 K in DSC scans) with the presence of a small amount of crystalline $\text{Ni}_{50}\text{Ti}_{50}$ (and possibly some crystalline Ni_3Ti) in the sample. Similar specimens examined in plane-view geometry with an Hitachi 7000 transmission electron microscope operated at 125 keV provide selected area diffraction patterns

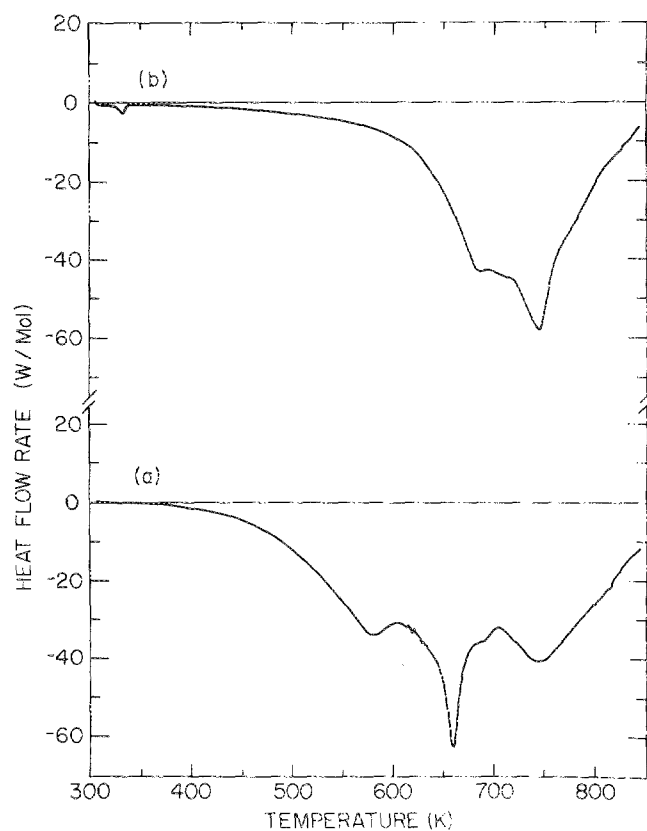


FIG. 1. The heat-flow rate as a function of temperature for a constant scan rate of 20 K/min, measured by means of differential scanning calorimetry. The samples were multilayered composites of approximate average stoichiometry $\text{Ni}_{40}\text{Ti}_{50}$ and $\text{Ni}_{47}\text{Zr}_{43}$ produced by co-deformation of the two metals. The initial thicknesses of the polycrystalline foils was 20 μm for Zr and Ti. Both composites were deformed similar amounts with a deformation of about 99%. The data are for: (a) Ni/Zr system and (b) Ni/Ti system.

[e.g. Figs. 2(d) and 2(e)] which indicate the same correlations between heat treatments and DSC scans, i.e., the formation of the amorphous phase upon heating followed by crystalline intermetallics at a temperature near 660 K.

The results of DSC measurements at different heating rates on numerous Ni/Ti composites indicate that the kinetics of the formation of equilibrium compounds are similar in both the Ni/Zr and the Ni/Ti codeformed, multilayered composites. It is only at approximately 660 K (in DSC scans at 10 K/min) that crystalline intermetallic compounds are observed to grow in the Ni-Ti system. Upon increasing the heating rate of Ni/Ti composites in DSC scans, the crystallization peak is observed to occur at progressively higher temperatures, providing some indication that the crystallization process is thermally activated. A Kissinger analysis³⁴ performed upon this data indicates that the activation energy for the formation and growth of $\text{Ni}_{50}\text{Ti}_{50}$ is 2.5 ± 0.2 eV, as compared to the activation energy (2.0 ± 0.1 eV) for the formation and growth of orthorhombic $\text{Zr}_{50}\text{Ni}_{50}$ observed in the Ni-Zr system.³⁰

Previous experiment^{35,36} at temperatures near 1000 K has indicated that Ni atoms diffuse an order of magnitude more rapidly in α -Zr than in α -Ti. We attempt to determine from our DSC measurements the relative rate of interdiffusion in amorphous Ni/Ti diffusion couples as compared to that in amorphous Ni/Zr diffusion couples.¹⁰⁻¹² We assume

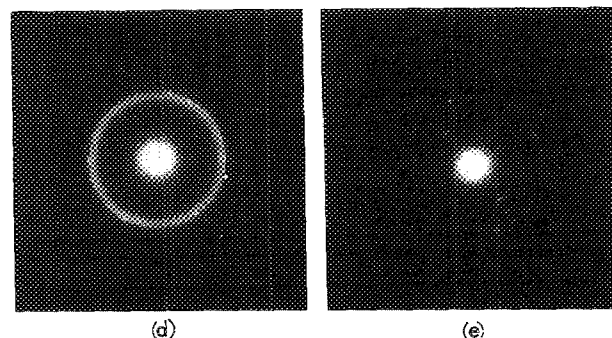
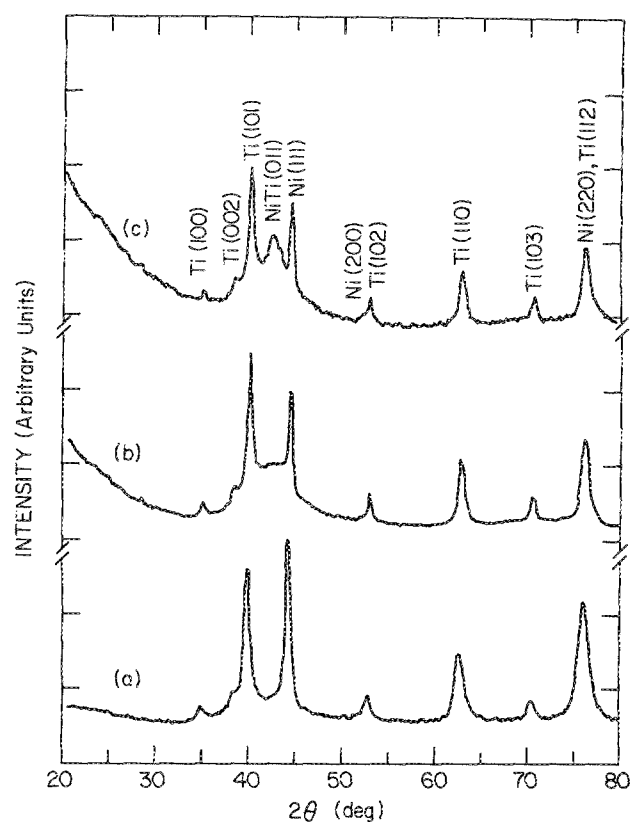


FIG. 2. (a)–(c) X-ray diffraction profiles (CuK α radiation) for a multilayered composite of Ni and Ti of average stoichiometry $\text{Ni}_{50}\text{Ti}_{50}$ (similar to sample of Fig. 1). (a) The as co-deformed sample. (b) The sample after being heated at 10 K/min to a temperature of 660 K and quenched to room temperature in the differential scanning calorimeter. (c) The sample after being heated at 10 K/min to a temperature of 670 K and quenched to room temperature in the differential scanning calorimeter. (d), (e) Similar specimens examined in plane-view geometry with an electron microscope operated at 125 keV to provide selected area diffraction patterns. (d) The sample after being heated at 10 K/min to a temperature of 660 K and quenched to room temperature in the differential scanning calorimeter. (e) The sample after being heated at 10 K/min to a temperature of 670 K and quenched to room temperature in the differential scanning calorimeter.

that the growth of amorphous material is one dimensional and diffusion controlled, and that the growing amorphous interlayer exhibits a linear concentration profile with constant interfacial compositions.³⁷ Then the following relationship³⁸ holds between the interlayer thickness X , the growth rate dX/dt , and the averaged interdiffusion coefficient D :

$$X \frac{dX}{dt} = \frac{\Delta c D}{x(1-x)}, \quad (1)$$

where Δc is the steady-state composition difference across the growing amorphous layer of average composition $\text{Ni}_x\text{Zr}_{1-x}$, and the ratio $\Delta c / [(x(1-x))]$ is close to one for both our systems. With H_f the enthalpy of formation of an amorphous alloy at the average composition of the growing amorphous layer, we can quantify the proportionality^{10-12,28} between the rate of heat release as measured by the DSC, dH/dt and the rate of growth of the amorphous layer, dX/dt :

$$\frac{dH}{dt} = \frac{A\rho H_f}{M} \frac{dX}{dt} = b \frac{dX}{dt}, \quad (2)$$

where A is the total interfacial area of the composite, ρ is the average density, and M the molar mass of an amorphous alloy at the average composition of the growing amorphous layer, and the proportionality constant $b = (A\rho H_f/M)$. Using Eqs. (1) and (2) we obtain:

$$H dH/dt \propto D, \quad (3)$$

where H is the integral of dH/dT from the initial reaction temperature to temperature T , and the proportionality constants for the Ni-Ti and Ni-Zr systems for samples of equal interfacial area A are found to be the same within error of about 10%. Therefore our DSC data for samples with equal values of A (e.g., Fig. 1) reflect the relative rates of growth in these two systems, and a simple analysis of our data (including the DSC data in Fig. 1) on the basis of Eq. (3) provide an estimate of the relative rates of interdiffusion in the Ni-Ti and Ni-Zr systems. We find that at temperatures near 600 K diffusion is more than an order of magnitude faster in the growing amorphous phase in the Ni-Zr system than in the Ni-Ti system, while a larger disparity is indicated at lower temperatures. At a temperature of 620 K we calculate the averaged interdiffusion coefficient in the growing amorphous Ni-Ti phase to be $D = 1 \times 10^{-14} \text{ cm}^2/\text{s}$.

Utilizing our measurement of the total heat release during the portion of the reaction identified with the formation of amorphous material we estimate the maximum thicknesses of amorphous material which was grown in our Ni/Ti composites before the formation of equilibrium compounds [e.g., grown upon heating to 650 K in Fig. 1(b)] to be on order of 100 Å, as compared to the limiting thickness of 1000 Å experimentally observed in Ni/Zr composites. The smaller thickness of amorphous material which can be grown by solid state reaction in the Ni-Ti system, combined with the indication that a disordered interface such as that produced by mechanical deformation facilitates these reactions, provides support for explanations for the relatively high degree of success experienced in the production of amorphous Ni-Ti by means of ball milling.²⁶⁻²⁹ Mechanically deforming powders by means of ball milling would most probably produce disordered interfaces. As previously suggested,²⁸ the continual creation of new Ni/Ti interfaces, and the relatively low temperatures produced in the ball mill, should allow for short diffusion distances. Thus solid state amorphization reactions may run under these conditions while being frustrated in a more ordered geometry with an interlayer thickness much greater than 100 Å.

We have investigated solid state reactions in mechanically deformed composites in both the Ni-Ti system and the Ni-Zr system. The growth of amorphous material in our Ni/

Ti composites is apparently facilitated by the relatively large degree of disorder induced in the metal layers, and therefore at the interfaces, by the mechanical deformation process. We find that amorphous material grows more slowly in the Ni-Ti system than the Ni-Zr system, while intermetallic compounds form at essentially the same rate in both systems. Thus the kinetic "window" allowing the formation of amorphous material in the Ni-Ti system is significantly narrower than that for the Ni-Zr system.

Valuable discussions with B. M. Clemens, B. Fultz, W. L. Johnson, W. J. Meng, C. Myers, K. Samwer, and S. Whittingham are gratefully acknowledged. We are grateful to C. Myers for utilization of x-ray diffraction facilities and to H. H. Eichelberger for assistance in transmission electron microscopy. This research was supported by the Research Corporation, Grant C-2587.

¹R. B. Schwartz and W. L. Johnson, Phys. Rev. Lett. **51**, 415 (1983).

²W. L. Johnson, Prog. Mater. Sci. **30**, 80 (1986).

³K. Samwer, Phys. Rep. **161**, 1 (1988).

⁴R. B. Schwarz and W. L. Johnson, J. Less-Common Met. **140**, 1 (1988).

⁵Y. T. Cheng, W. L. Johnson, and M.-A. Nicolet, Appl. Phys. Lett. **47**, 800 (1985).

⁶H. Hahn and R. S. Averback, Phys. Rev. B **37**, 6537 (1988).

⁷A. M. Vredenberg, J. F. M. Westendorp, F. W. Saris, N. M. van der Pers and Th. H. de Keijser, J. Mater. Res. **1**, 774 (1986).

⁸W. J. Meng, C. W. Nieh, E. Ma, B. Fultz, and W. L. Johnson, J. Mater. Sci. Eng. **97**, 87 (1988).

⁹H. Hahn, R. S. Averback, and S. J. Rothman, Phys. Rev. B **33**, 8825 (1986).

¹⁰E. J. Cotts, W. J. Meng, and W. L. Johnson, Phys. Rev. Lett. **57**, 2295 (1986).

¹¹L. Schultz, in *Rapidly Quenched Metals*, edited by S. Steeb and H. Warlimont (North-Holland, Amsterdam, 1984), p. 551.

¹²R. J. Highmore, J. E. Evetts, A. L. Greer, and R. E. Somekh, Appl. Phys. Lett. **50**, 566 (1987).

¹³W. J. Meng, B. Fultz, E. Ma, and W. L. Johnson, Appl. Phys. Lett. **51**, 661 (1987).

¹⁴J. C. Gachon and J. Hertz, Calphad **7**, 1 (1983).

¹⁵A. W. Weeber, P. I. Loeff, and H. Bakker, J. Less-Common Met. **145**, 293 (1988).

¹⁶K. H. Buschow, J. Phys. F **14**, 593 (1984).

¹⁷Z. Altounian, Tu Guo-hua, and J. O. Strom-Olsen, J. Appl. Phys. **54**, 3111 (1983).

¹⁸K. H. Buschow, J. Phys. F **13**, 563 (1983).

¹⁹K. Hoshino, R. S. Averback, H. Hahn, and S. J. Rothman, J. Mater. Res. **3**, 55 (1988).

²⁰W. J. Meng, E. J. Cotts, and W. L. Johnson, in *Interfaces, Superlattices, and Thin Films*, edited by J. D. Dow and I. K. Schuller, Mater. Res. Soc. Symp. Proc. **77** (Materials Research Society, Pittsburgh, 1987).

²¹B. M. Clemens, J. Appl. Phys. **61**, 4525 (1987).

²²B. M. Clemens, Phys. Rev. B **33**, 7615 (1986).

²³B. M. Clemens and J. G. Gay, Phys. Rev. B **35**, 9337 (1987).

²⁴G. C. Wong, W. L. Johnson, and E. J. Cotts, J. Mater. Res. **5**, 488 (1990).

²⁵J. F. Jongste, M. A. Hollanders, B. J. Thijsse, and E. J. Mittemeijer, Mater. Sci. Eng. **97**, 101 (1988).

²⁶R. B. Schwarz and C. C. Koch, Appl. Phys. Lett. **49**, 146 (1986).

²⁷R. B. Schwarz and R. R. Petrich, J. Less-Common Met. **140**, 171 (1988).

²⁸R. B. Schwarz, R. R. Petrich, and C. K. Saw, J. Non-Cryst. Solids **76**, 281 (1985).

²⁹E. Hellstern and L. Schultz, Appl. Phys. Lett. **48**, 124 (1986).

³⁰E. J. Cotts, G. C. Wong, and W. L. Johnson, Phys. Rev. B **37**, 9049 (1988).

³¹M. Atzmon, J. D. Verhoeven, E. D. Gibson, and W. L. Johnson, Appl. Phys. Lett. **45**, 1052 (1984).

³²S. Enzo, L. Schiffrini, L. Battezzati, and G. Cocco, J. Less-Common Met. **140**, 129 (1988).

³³C. M. Jackson, H. J. Wagner, and R. J. Wasilewski, NASA Technology

Subnanosecond far infrared photoconductivity from a GaAs/AlGaAs multiquantum well

R. E. M. de Bekker

*Max Planck Institut für Festkörperforschung, Hochfeldmagnetlabor, Boîte Postale 166X,
38042 Grenoble Cedex, France*

J. M. Chamberlain

Physics Department, Nottingham University, Nottingham, NG7 2RD, United Kingdom

L. M. Claessen^{a)} and P. Wyder

*Max Planck Institut für Festkörperforschung, Hochfeldmagnetlabor, Boîte Postale 166X,
38042 Grenoble Cedex, France*

M. B. Stanaway, R. T. Grimes, M. Henini, and O. H. Hughes

Physics Department, Nottingham University, Nottingham, NG7 2RD, United Kingdom

G. Hill

Department of Electronic Engineering, Sheffield University, Sheffield, S1 3JD, United Kingdom

(Received 21 December 1989; accepted for publication 3 May 1990)

The far infrared (FIR) photoconductivity of GaAs/AlGaAs multiquantum wells (MQWs) doped with silicon has been investigated. The spectral response is consistent with extrinsic photoconductivity from shallow donors with an effective Rydberg of approximately 10.5 meV. The time-resolved photoconductivity due to stimulation with a cavity-dump FIR laser is measured. Subnanosecond rise and decay times are implied for the MQWs investigated; these times are shorter than for the corresponding bulk cases. Possible effects of geometric confinement on recombination rates are discussed. For a 150-period MQW, the responsivity at 118 μm is approximately 10^5 V W^{-1} .

In this communication, we describe a study of the continuous wave (cw) and time-resolved (TR) far infrared (FIR) photoconductive response of silicon-doped GaAs/AlGaAs multiquantum wells (MQWs). The TR behavior on the nanosecond scale suggests that appropriately doped GaAs/AlGaAs MQW structures may have some potential as fast, sensitive detectors of long wavelength ($\lambda \approx 100 \mu\text{m}$) radiation.

It is now well established, both experimentally and theoretically,^{1,2} that the binding energy of an electron to a hydrogenlike impurity in a MQW is shifted from the bulk value when the effective Bohr radius approaches the well width. It is of interest to determine if recombination rates for electrons bound to shallow impurities in a MQW are in any way affected by reduced dimensionality. It is suggested that the recombination rates³ for acoustic-phonon-assisted processes would increase due to reduction of the number of phonon

wavelengths within the spatial extent of the effective Bohr orbit, the size of which is reduced by confinement.

We report measurements of the FIR photoconductive response for 150-period MQW structures at 4.2 K, using short pulses ($< 10 \text{ ns}$) generated by a novel cavity-dump laser technique.⁴ Figure 1 shows the layer structure for a typical sample. A 150-period structure was chosen to ensure a convenient photoconductive signal size for detection: the layer dimensions were chosen to give an effective donor binding energy appropriate to the energy of the FIR laser pulse. A relatively thick (0.5- μm) region of AlGaAs is present between the wells and the high-mobility GaAs buffer layer to ensure that the observed photoconductive response originates from electrons bound to shallow impurities in the wells and not in the buffer region. This was confirmed experimentally in a cw magnetospectroscopy measurement by observation of the magnetic field shift and angle dependence⁵ of the $1s-2p_+$ transition. Au-Ge-Ni ohmic contacts were formed to the layers, and an interdigitation pattern was used to reduce the sample resistance to convenient values for matching to detection circuitry.

^{a)} Present address: Philips Research Laboratories, P.O. Box 80.000, 5600 JA Eindhoven, The Netherlands.