AD-A094 400   AIR FORCE INST OF TECH WRIGHT-PATTERSON AFB OH   SCHOO--ETC   F/G 7/4
PHOTOLUMINESCENCE STUDY OF THERMAL CONVERSION IN GALLIUM ARSENI--ETC(U)
DEC 80   J M ANDERSON
UNCLASSIFIED   AFIT/GEO/PH/80-1   NL

1 OF 1
AD A
094400

END
DATE
FILMED
2-81
DTIC

AD A094400

II ①

APPROVED FOR PUBLIC RELEASE AFR 190-17.

14 JAN 1981

Fredric C. Lynch

**FREDRIC C. LYNCH, Major, USAF**
**Director of Public Affairs**

Air Force Institute of Technology (ATC)
Wright-Patterson AFB, OH 45433

# PHOTOLUMINESCENCE STUDY OF THERMAL CONVERSION IN GALLIUM ARSENIDE

THESIS

AFIT/GEO/PH/80-1

John M. Anderson
1st Lt. USAF

DTIC

AFIT/GEO/PH/80-1

# PHOTOLUMINESCENCE STUDY OF THERMAL CONVERSION IN GALLIUM ARSENIDE

THESIS

PRESENTED TO THE FACULTY OF THE SCHOOL OF ENGINEERING
OF THE AIR FORCE INSTITUTE OF TECHNOLOGY
AIR UNIVERSITY (ATC)
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

BY
JOHN M. ANDERSON
FIRST LIEUTENANT USAF
GRADUATE ELECTRO-OPTICS
DECEMBER 1980

Approved for public release; distribution unlimited.

# Preface

Although the scope of this study was limited by time and sample availability, I believe it to be one of the most comprehensive studies of thermal conversion yet performed. I would like to thank Dr. Robert Hengehold for his guidance during this project and for his suggestions in several problem areas. I am also very grateful to Jim Miskimen and Ron Gabriel of the AFIT Physics Laboratory for their technical assistance and to doctoral student Mike Sydenstricker who took time out from his own research to help me learn to operate the photoluminescence equipment. I would also like to thank Dr. Theodore Luke who, although not my thesis advisor, took time to help familiarize me with the experimental equipment. Thanks are due to Gernot Pomrenke of the Air Force Wright Aeronautical Laboratories (AFWAL) for providing the necessary samples and electrical measurements and to Charles Geesner and Jim Ehret, also of AFWAL, for their patience while I learned to anneal the samples. Finally, I would like to thank my wife, Lora, for her understanding and patience during this project.

John M. Anderson

# Contents

## List of Figures

# List of Tables

## Abstract

A photoluminescence study was made of undoped and Cr-doped GaAs annealed in three different atmospheres: Ar, $N_2$, and $H_2$. The purpose of this study was to determine the causes of thermal conversion and to examine the effects of different annealing atmospheres on this problem.

It was found that conversion can be due to any of a number of causes, rather than to one common cause or combination of causes as was previously believed. Conversion in the samples studied was associated with carbon impurities in undoped samples and with silicon in doped samples. Although manganese was found to be present in many samples, no clear association of manganese with type conversion was found. It was found that annealing under nitrogen gas was the most effective way of maintaining a semi-insulating surface layer.

# PHOTOLUMINESCENCE STUDY OF THERMAL CONVERSION IN GALLIUM ARSENIDE

## I Introduction

### Background

Thin homogeneous epitaxial layers of GaAs are widely required for the fabrication of microwave devices and integrated circuits. The growth of these epitaxial layers requires the heating of the GaAs substrate to temperatures in the region of 750°-1100°C, a process which often causes the formation of an interfacial layer with an electrical character that contrasts sharply with both epilayer and substrate (Ref 1:1). Specifically, a low-resistivity surface layer of either n or p carrier type is produced. This phenomenon is known as thermal conversion, and has been the subject of much research since its discovery in 1960 because of its disastrous effect on the performance of GaAs electronic devices. The reason for this conversion is still not understood, although several explanations have been advanced.

Recently the Air Force Wright Aeronautical Laboratories (AFWAL) began a study of the thermal conversion problem in GaAs, with particular emphasis on the conversion of samples annealed with a silicon nitride ($Si_3N_4$) encapsulant. The investigation as planned will use a wide range of characterization methods such as sheet, profile, and temperature dependent Hall measurements, deep level transient spectroscopy, secondary ion mass spectroscopy (SIMS), and spark source in addition to this photoluminescence study performed at AFIT.

## Problem

The objectives of this study are to obtain photoluminescence spectra of converted and unconverted samples before and after annealing, to use these spectra to identify the impurities and other defects which are present in the samples, and to compare the spectra of converted and unconverted samples and their substrates to determine the possible causes of thermal conversion. Further, this study will try to identify possible ways to prevent or limit conversion in the future.

# II Theory and Previous Work

## Characteristics of GaAs

The semiconductor GaAs is one of the intermetallic compounds which are formed between the elements of group III and group V of the periodic table. Like other III-V semiconductors, it crystallizes in the zincblende structure and has physical properties very much like those of the covalent group IV elements in many respects. The III-V semiconductors are, however, slightly ionic in character, a fact which is responsible for most of the differences in the properties of the III-V compounds and the group IV covalent semiconductors. The III-V semiconductors are therefore characterized by high electron mobility and mobility ratio (Ref 2:371).

## Photoluminescence

Photoluminescence occurs when an electron-hole pair, formed by optical excitation of the material, recombines and subsequently emits energy in the form of light. The simple energy band diagram in figure 1 on the following page illustrates five different kinds of recombinations: band-to-band, free exciton, bound exciton, conduction band-to-acceptor, donor-to-valence band, and donor-to-acceptor. In this diagram, the conduction band represents the excited

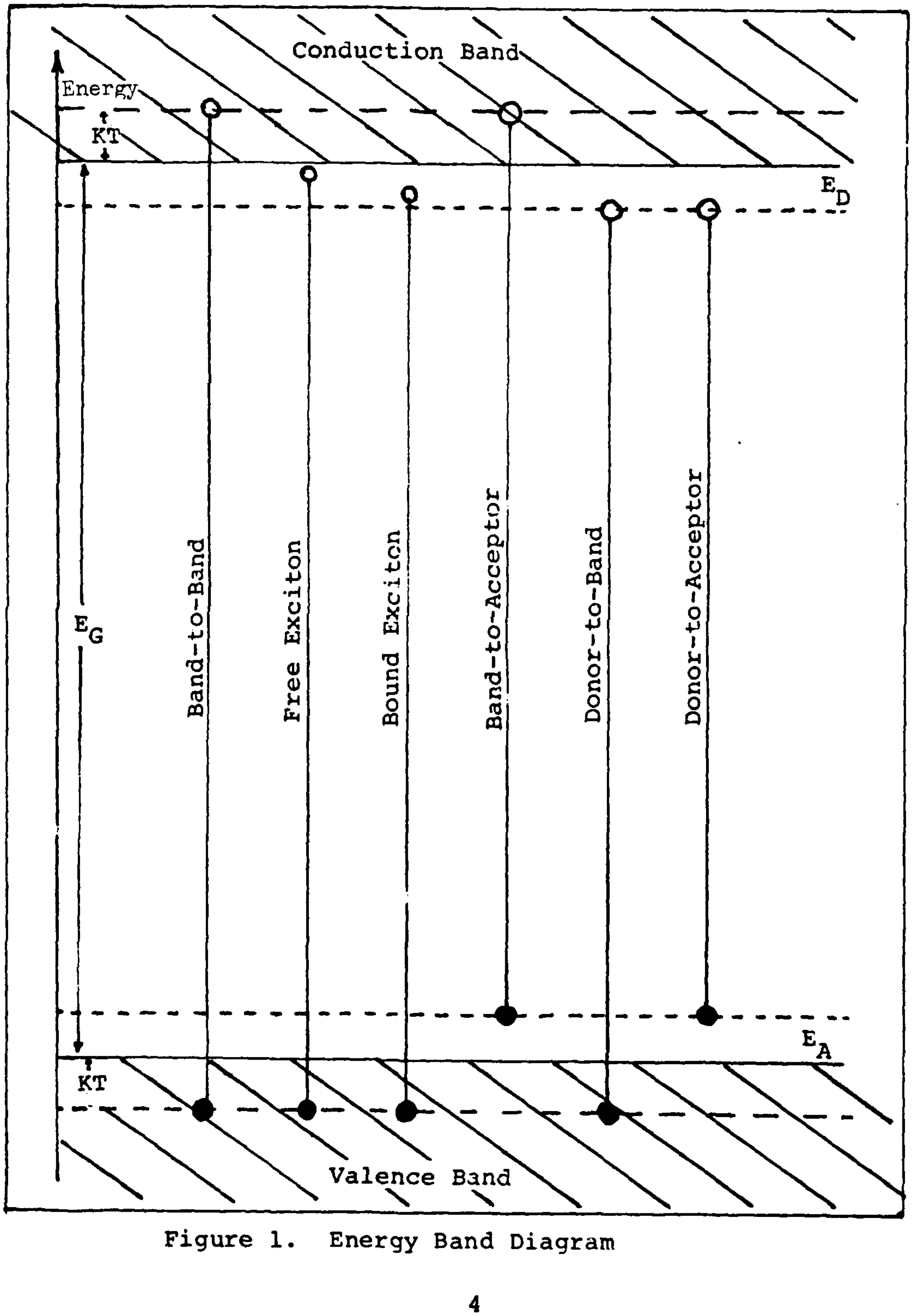

Figure 1. Energy Band Diagram

states to which electrons can be raised from their normal ground state. The ground state is represented by the valence band, and the region between the valence and conduction bands is the energy gap. Energy levels within the gap are caused by the presence of excitons, impurity atoms, and crystal defects.

Band-to-Band Recombination. Band-to-band transitions are characterized by low energy thresholds at bandgap energy, which is located at 1.52 eV for GaAs at 20°K. They are identified by a temperature dependent high-energy tail with a low energy edge cutoff at bandgap energy (Ref 3:124). At low temperatures, however, free electrons and holes tend to bind together by electrostatic force, thus minimizing the presence of band-to-band recombinations.

Exciton Recombination. Due to the unstable nature of the exciton, the electron and hole will eventually recombine, emitting a photon. In the presence of impurities, an exciton may become bound to a donor or acceptor center. In these cases the energy emitted is less than that for a free exciton by an amount equal to the binding energy of the exciton to the impurity (Ref 3:114-118). The bound exciton recombination energies for GaAs at 2°K have been found to lie between 1.512 and 1.515 V with the free exciton at 1.516 eV (Ref 4:341-351).

Band-to-Impurity Recombination. This transition involves the recombination of a free electron or hole with an electron or hole bound to an impurity center. The luminescence peaks are characterized by a shape broader than that of a bound exciton transition, and are located at an energy level given by the following equation (Ref 5:744):

$$E = E_g - E_b + KT \pm nE_p \tag{1}$$

where

$E_g$ = band gap energy

$E_b$ = impurity binding energy

$K$ = Boltzmann's constant

$T$ = absolute temperature

$n$ = number of optical phonons

$E_p$ = optical phonon energy

Donor-Acceptor Recombination. The final transition involves the recombination of an electron bound to a donor impurity with a hole bound to an acceptor. The energy of the emitted radiation is given by the following equation (Ref 5:743):

$$E = E_g - (E_b + E_d) \pm nEp + \frac{e^2}{kr} \tag{2}$$

where

$E_a$ = acceptor binding energy

$E_d$ = donor binding energy

e = electronic charge

k = static dielectric constant

r = separation between sites

Since many discrete values of r may occur, the characteristic shape of the donor-acceptor pair peak is a rather broad peak which is the envelope of the unresolvable sharp peaks.

Phonon Coupling. In equations (1) and (2) above, the term nEp represents discrete amounts of energy which can be given to or absorbed from the crystal lattice in the form of lattice vibrations. These quanta of energy are called phonons, and are responsible for replicas of impurity-related peaks. The two most commonly observed types of phonons are the longitudinal optical (LO) phonon and the transverse acoustic (TA) phonon, of which the LO phonon coupling is by far the stronger because of the polarization field associated with it. For the LO phonon, $E_p$ = 36 meV (± 2meV), so LO phonon coupled peaks are separated by 36 meV. For the TA phonon, $E_p \simeq 9$ meV. Figure 2 shows the LO phonon coupling associated with four acceptors in GaAs at 20°K (Ref 4:387-388).

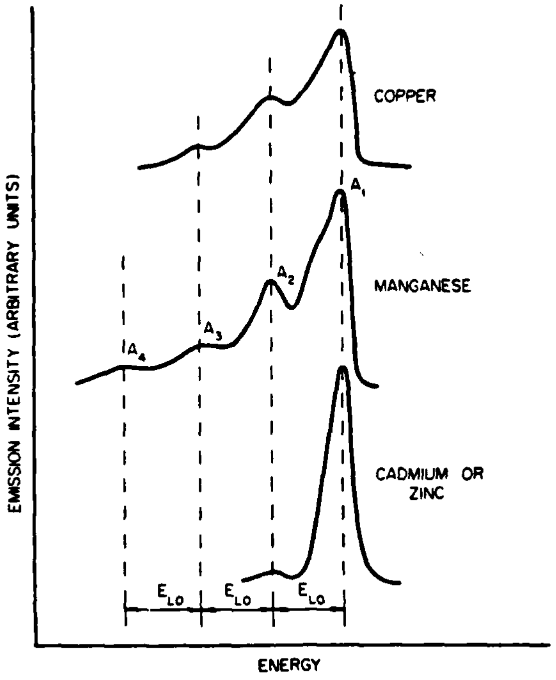

Figure 2 Phonon Coupling for Four Acceptors (Ref 4:388)

For the shallow simple acceptors Zn and Cd , the coupling is weak and only one LO replica can be seen. For the deeper centers Mn and Cu the coupling is much stronger and two or three replicas can be seen. The shoulder on the edge of the zero-phonon Mn line corresponds to the first TA phonon replica.

## Summary of Previous Work

The thermal conversion problem was first reported in 1960 in two independent papers by J.T. Edmond (Ref 6:1428) and J.J. Wysocki (Ref 7:1686). Both considered copper to be responsible and believed that the copper came from the quartz ampule used in heating (Ref 6:1428) or the reagent used in the cleaning (Ref 7:1692).

A photoluminescence study in 1968 by C.J. Hwang put the blame for conversion of GaAs on copper and silicon (Ref 8: 5347). This study used undoped GaAs crystals, annealed in a vacuum at temperatures ranging from 600° to 1100°C. Two lines were associated with the converted crystals: a band to shallow acceptor recombination at 1.486 eV and a band to copper acceptor recombination at 1.356 eV. The conclusion was that conversion was caused by copper for annealing temperatures below 870°C and by copper and silicon for temperatures above 900°C.

A cathodoluminescence study in 1971 by Chang, Esaki, and Tsu examined undoped and selenium doped crystals annealed in arsenic at temperatures ranging from 600° to 1100°C. It was concluded that silicon and oxygen related vacancies were responsible for the conversion and that fast-diffusing species such as copper could be ruled out (Ref 9:143).

In 1977, a photoluminescence study by the Naval Research Laboratory examined chromium-doped GaAs heat-treated at 750°C under hydrogen gas. The converted samples showed the emergence of a peak at 1.413 eV and an increase in the height of a peak at 1.493 eV. The 1.413 eV peak was attributed to arsenic-vacancy complexes and the 1.493 eV peak was assigned to carbon impurities, which were indicated to be responsible for the conversion of the material (Ref 1: 1-3). Later in 1977 the Naval Research Laboratory published another photoluminescence study in which the samples were heat treated at 900°C. In this study the 1.413 eV peak increased in relative intensity as compared to the previous study, and was attributed to the formation of carbon donor centers and the compensation or reduction in density of acceptors formed by the substitution of C atoms on As sites (Ref 10:214).

In a 1977 photoluminescence paper by Hallais et al (Ref 11:226), semi-insulating GaAs was annealed for 30 minutes at 750°C under three atmospheres: hydrogen, vacuum, and argon. In argon no change appeared in the photoluminescence spectra and thermal conversion was not experienced. Conversion did take place in both hydrogen and vacuum, although the spectra for the vacuum samples did not change for the range examined (1.52 - 1.30 eV). For the samples annealed under hydrogen a strong line at 1.409 eV was observed which was identified with a manganese impurity, although no explanation for the source of the manganese could be found. For vacuum-annealed samples, conversion was attributed to gallium vacancy formation during annealing.

At the same time as the Hallais study, a study by Zucca investigated the surface conversion of Cr-doped GaAs annealed in hydrogen at temperatures between 700 - 775°C (Ref 12:233). Zucca also identified manganese as the cause of conversion and suggested that manganese might be present in all semi-insulating GaAs and be activated by the heat treatment. In addition to the evidence implicating manganese, Zucca also found an acceptor peak located at 1.491 eV which corresponded to several impurities: beryllium, magnesium, carbon, and zinc (Ref 12:234).

It is well-known that, when heat-treated, chromium diffuses outward in semi-insulating GaAs. In a 1979 paper by Ohno _et al_, it was suggested that the outward diffusion of chromium, along with oxygen, was responsible for the thermal conversion of semi-insulating GaAs (Ref 13:8226). The presence of oxygen was explained by noting that, during growth of the chromium doped crystal, oxygen was unintentionally doped into the sample.

In a recent paper from the Naval Research Laboratory, semi-insulating GaAs was annealed under hydrogen and studied by photoluminescence, secondary ion mass spectrometry (SIMS), and transport measurements. The SIMS measurements resulted in the direct chemical identification of manganese near the heated surface. This, combined with the appearance of the 1.409 eV manganese line in the photoluminescence experiment, identified manganese as the cause of the surface conversion. This paper also determined that the manganese layers were not introduced by contamination from external sources, but were due to native manganese impurities (Ref 14).

The problem of thermal conversion has been the subject of much research over the past twenty years, and a number of papers identifying possible causes of thermal conversion have been written. However, these papers are in general disagreement, and the cause of thermal conversion remains unknown. Some of the most popular suspects are: carbon, copper, silicon, oxygen, manganese, and chromium impurities, and both gallium and arsenic vacancies.

## III Equipment, Procedure, and Sample Information

The experimental portion of this study consisted of obtaining photoluminescence spectra of GaAs samples before and after annealing. These spectra were then compared with the electrical data obtained from Hall effect measurements. Samples were representative of a variety of annealing conditions and were furnished by AFWAL (Avionics Laboratory).

### Equipment

The basic equipment for this study is shown in figure 3 on the following page. The main components included a temperature controlled sample environment, illuminating source, signal processing elements, and signal recorders.

Sample Environment. The sample environment was maintained at a pressure of approximately $10^{-7}$ torr by a Welch Scientific Company model 1402 mechanical pump and by a pair of Edwards High Vacuum Ltd. oil diffusion pumps. The pressure was measured by a Varian ionization gauge with a Granville-Phillips ionization gauge controller. The samples were cooled by liquid helium which was transferred from a liquid helium dewar to the sample environment at a constant flow rate using an Air Products Heli-tran liquid helium transfer unit. Minimum possible temperatures ranged from 18-23°K with this system.

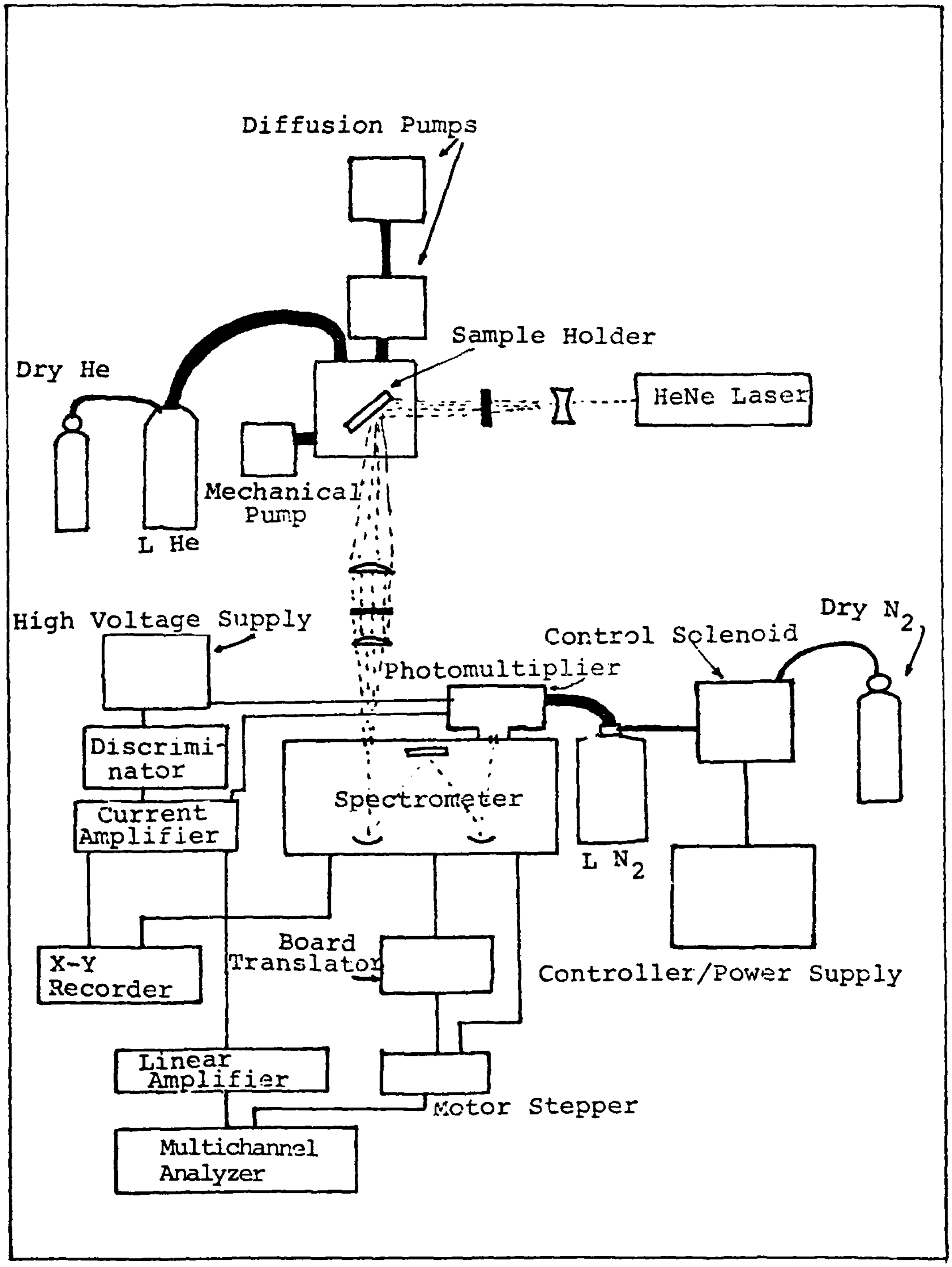

Figure 3 Photoluminescence Equipment

The samples were mounted on a copper sample block located at the end of the helium transfer unit. Each of four samples was held in place by a copper mask having a central circular hole with a diameter of 2 mm. The samples were held by the masks so that only their central areas were exposed to the laser beam. A GaAs temperature sensing diode was located in the center of the sample block, and served as the thermometer for the samples.

Illumination Source and Optics. The samples were excited by a Spectra-Physics model 124 HeNe laser. This laser provided 11 mW with a beam diameter at the $\frac{1}{e^2}$ points of .9 mm. Before striking the sample the laser beam was filtered by a high-pass filter and diverged by a biconcave lens. The beam diameter at the sample was approximately 2 mm so that all the visible portion of the sample was covered.

Luminescence from the sample was collected and focused on the spectrometer entrance slit by two plano-convex lenses. The first lens had a focal length of 10cm and was located approximately 10 cm from the sample. The second lens had a focal length of 25 cm and was located 25 cm from the entrance slit. The luminescence from the sample was filtered by a low pass filter to remove the reflected laser light before entering the spectrometer.

Signal Processing. A Spex model 1702 Czerny-Turner scanning spectrometer was used to disperse the signal. The grating used was blazed at 5000Å with 1200 grooves/mm. Scanning speed, which was controlled by the spectrometer's internal motor plus a motor stepper drive ranged from 17.5 to 104 Å/min, and slit widths ranged from 0.1 to 0.7 mm.

The dispersed signal was detected by a RCA C70007A S-1 photomultiplier cooled to -80°C by liquid nitrogen in a Products for Research photomultiplier housing. The photomultiplier was supplied a 1350V bias from a Princeton HVS-1 high voltage power supply. The photomultiplier output was processed by a Keithly model 427 current amplifier which provided gain of $10^4$ with a rise time of 300 msec

The final output signal was recorded by two instruments: a Moseley model 7000A X-Y chart recorder and a Hewlett-Packard 5400A multi-channel spectrum analyzer, with attached paper tape punch and read units. Line positions on the multichannel analyzer could be read to an accuracy of better than 1meV in all cases.

## Procedure

Sample Mounting. The sample mount was removed from the vacuum chamber by first filling the chamber with dry nitrogen and closing the high vacuum valve. The end of the liquid helium transfer unit could then be pulled out of the vacuum chamber with the copper sample block attached. One sample was then placed under each of the four sample masks, after first applying a small amount of GaInSn alloy to assure thermal contact with the copper block.

Evacuation and Cryogenics. After the sample mount was returned to the vacuum chamber it was evacuated to approximately $5 \times 10^{-6}$ torr by using first the mechanical rough pump and then the diffusion pump. The flow of liquid helium was then started by forcing dry helium into the liquid helium dewar. All photoluminescence data was taken at the minimum attainable temperature, which was typically 20°K.

Alignment. Alignment of the laser beam consisted of positioning the laser so that the beam struck the sample to be studied and adjusting the position of the concave lens so that the beam size at the sample matched the aperture size of the sample mask. Luminescence from the sample was focused on the spectrometer entrance slit by adjusting the two plano-convex lenses so that maximum deflection was obtained on the X-Y recorder.

Data Collection. Data collection was performed simultaneously by the X-Y recorder, which was used mainly to monitor the experiment while in progress, and by the multichannel spectrum analyzer. The scan in most instances was started at 800nm with the spectrometer slits in their narrowest position and an argon calibration lamp between the two plano-convex lenses. After the 800.616 nm argon line had been recorded, the lamp was removed and the spectrometer slits dialed to the desired width. Peak position channel numbers on the spectrum analyzer were compared to the channel number of the 800.616 nm line to determine peak positions in terms of energy or wavelength.

Scans for all samples were performed from 800 - 977.8 nm. Since the spectrum analyzer allowed the display to be expanded or contracted both vertically and horizontally, the basic scan was usually quite adequate to resolve the peaks involved. However, on those occasions when more separation was needed, an additional scan over a shorter range was performed. Scanning spreads therefore varied from 22.2 nm to 177.8 nm.

Spectra recorded on the spectrum analyzer were transferred to paper tape using the spectrum analyzer's tape-punch unit. The paper tapes were converted to punched computer cards and then to the luminescence spectra plots which appear in this thesis.

## Sample Data

The samples used in this study were provided to AFIT by AFWAL/AA (Avionics Laboratory). Undoped GaAs samples originated from Westinghouse, while chromium doped samples were produced by Crystal Specialties, Inc. Samples were examined by photoluminescence before and after annealing under a variety of conditions.

Table 1 on the following page shows the annealing conditions for each sample examined.

All $Si_3N_4$, encapsulants and vapour phase epitaxial (VPE) buffer layers were deposited by AFWAL. The $Si_3N_4$ caps were applied by plasma deposition at 300°C to a thickness of 100 nm. Due to another experiment within AFWAL the buffer layer growth chamber contained small amounts of tin which, was found to be present in all VPE buffer layer samples.

All samples were annealed face-down under hydrogen, argon, or nitrogen gas for 20 minutes. Most samples were annealed at 850°C, although encapsulated Cr-doped samples were also annealed at 750, 800, and 900°C.

Hall measurements were performed by AFWAL on all samples. The principle purposes of the Hall measurements were to determine what change in resistivity took place due to annealing and whether the sample converted from n to p-type. The resistivity and type of each sample is shown in table 1. Under the heading "Surface Type", four types are given: "n", "p", "SI", and "n,p" represent n-type or p-type surfaces as determined by Hall effect measurements. The symbol "SI" represents a semi-insulating surface, "n,p" means that mixed conductivity was observed, but the sample did not convert to p-type.

# TABLE 1

## SAMPLE CONDITIONS

| SAMPLE | | $Si_3N_4$ Cap | Annealing Atmosphere | Conditions Temp (°C) | Surface Type. | Resistivity |
|---|---|---|---|---|---|---|
| Undoped GaAs | W8/20 | | | | N | ~ E(8) |
| | | | H2 | 850 | P | 2.016 E (4) |
| | | X | Ar | 850 | N,P | 3.761 E (6) |
| | WBN6/24 | | | | N | ~ E(8) |
| | | | H2 | 850 | P | 1.122 E (4) |
| | | X | Ar | 850 | P | 1.565 E (5) |
| Cr-doped GaAs | CS4679/66 | | | | SI | ~ E(10) |
| | | | H2 | 850 | P | 6.481 E (3) |
| | CS4679/73 | | | | SI | 8.170 E (8) |
| | | | H2 | 850 | P | 1.155 E (4) |
| | CS4679/78 | | | | SI | ~ E(10) |
| | | | H2 | 850 | P | 2.846 E (4) |
| | CS4679/77 | | | | SI | ~ E(10) |
| | | | H2 | 850 | P | 2.596 E (4) |
| | | | Ar | 850 | N,P | 1.284 E (4) |
| | | | N2 | 850 | N,P | 3.360 E (8) |
| | CS4679/75 | | | | N,P | 1.164 E (10) |
| | | | H2 | 850 | P | 1.364 E (4) |
| | | | Ar | 850 | N,P | 6.756 E (4) |
| | | | N2 | 850 | N,P | 5.847 E (7) |
| | | X | H2 | 750 | N,P | 1.482 E (8) |
| | | X | H2 | 800 | N,P | 2.1916 E (8) |
| | | X | H2 | 850 | N,P | 8.173 E (4) |
| | | X | H2 | 900 | N,P | 5.699 E (3) |
| | | X | Ar | 750 | N,P | 6.108 E (7) |
| | | X | Ar | 800 | N,P | 9.727 E (7) |
| | | X | Ar | 850 | N,P | 6.372 E (3) |
| | | X | Ar | 900 | N,P | 2.053 E (3) |
| | CS4679/75 with VPE Buffer Layer | | | | SI | 9.322 E (7) |
| | | | H2 | 850 | P | 6.186 E (3) |
| | | | Ar | 850 | P | 3.088 E (6) |
| | | | N2 | 850 | P | 1.355 E (5) |
| | | X | H2 | 850 | P | 9.971 E (4) |
| | | X | Ar | 850 | P | 9.654 E (5) |

# IV Results and Analysis

The spectral results for the samples shown in Table 1 are presented in this section. For purposes of discussion, the samples are divided into three general categories: Cr-doped GaAs, Cr-doped GaAs with an epitaxial layer, and undoped GaAs.

## Cr-doped GaAs

Unannealed Samples. Five Cr-doped samples were examined before annealing. The spectrum of one of these is shown in figure 4; the other four spectra are virtually identical and are shown in the appendix. This spectrum shows an exciton peak at 1.514 eV, a peak at 1.495 eV which is identified as a band-to-C acceptor recombination (Ref 15:1051), and a peak at 1.489 eV which is identified as a band-to-Zn acceptor recombination (Ref 4:350, Ref 15:1051). These lines are followed by three LO phonon replicas at 1.465 eV, and 1.431 eV. A pair of peaks at 1.356 eV and 1.320 eV are identified as a Cu acceptor - As vacancy and LO phonon replica (Ref 4:384-385).

Samples Annealed in $H_2$. Figure 5 shows a typical spectrum for a Cr-doped sample annealed in $H_2$; the spectra for the other four $H_2$-annealed samples are shown in the appendix. This spectrum shows an exciton line at 1.514 eV, a peak at

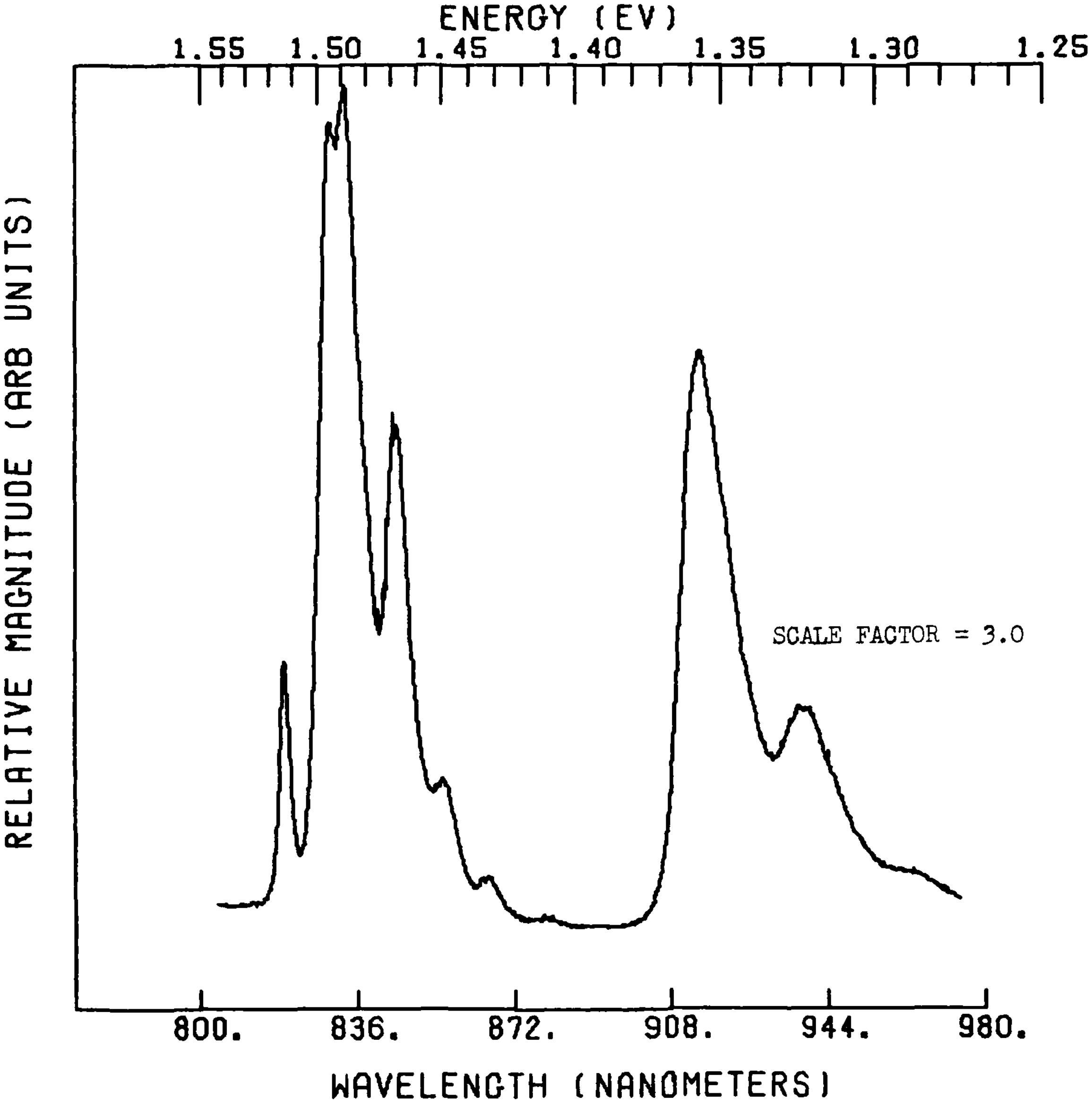

Figure 4. Photoluminescence of Sample CS4679/75 Before Annealing

1.484 eV, a small peak at 1.448 eV, and a series of peaks at 1.408 eV, 1.400 eV, 1.372 eV, 1.357 eV, and 1.336 eV. The last series of peaks is identified as an acceptor-As vacancy peak followed by TA and LO phonon replicas. The appearance of this series is predicted by several papers which associate the lines with a Mn acceptor and label Mn as the cause of conversion (Ref 12:233-234, Ref 14:1-3). The peak at 1.484 eV is believed to be a band-to-Si acceptor recombination (Ref 15:1051) followed by an LO phonon replica at 1.448 eV. All these samples converted to p-type, as can be seen in Table 1.

A temperature study was performed on $Si_3N_4$ encapsulated Cr-doped samples by annealing in $H_2$ for 20 minutes at 750, 800, 850, and 900°C. Figures 6-9 show the spectra of these samples. None of these converted to p-type, but the samples at 850° and 900° suffered a drastic reduction in resistivity, as can be seen in table 1, and the samples at 750° and 800° showed damage peaks within the acceptor peak. These spectra show the growth of the vacancy peak at 1.408 eV which appears at 800°, grows slightly larger at 850°, and then disappears completely in the 900° sample. Also evident is the growth with increasing temperature of the 1.494 eV Si peak, although it does not reach the size that it does in the uncapped samples.

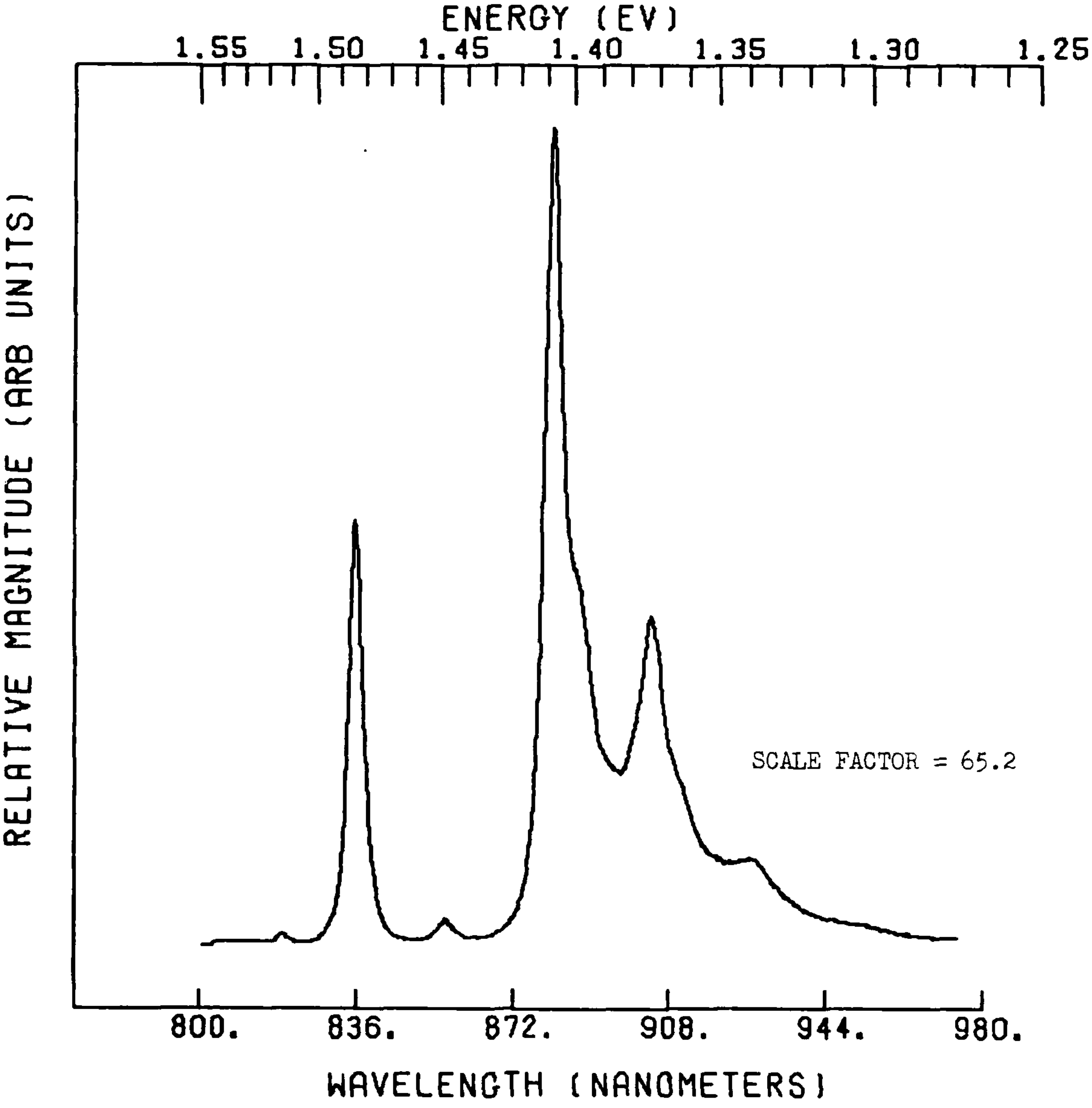

Figure 5. Photoluminescence of Sample CS4679/75 After Annealing in $H_2$ at 850°C for 20 minutes.

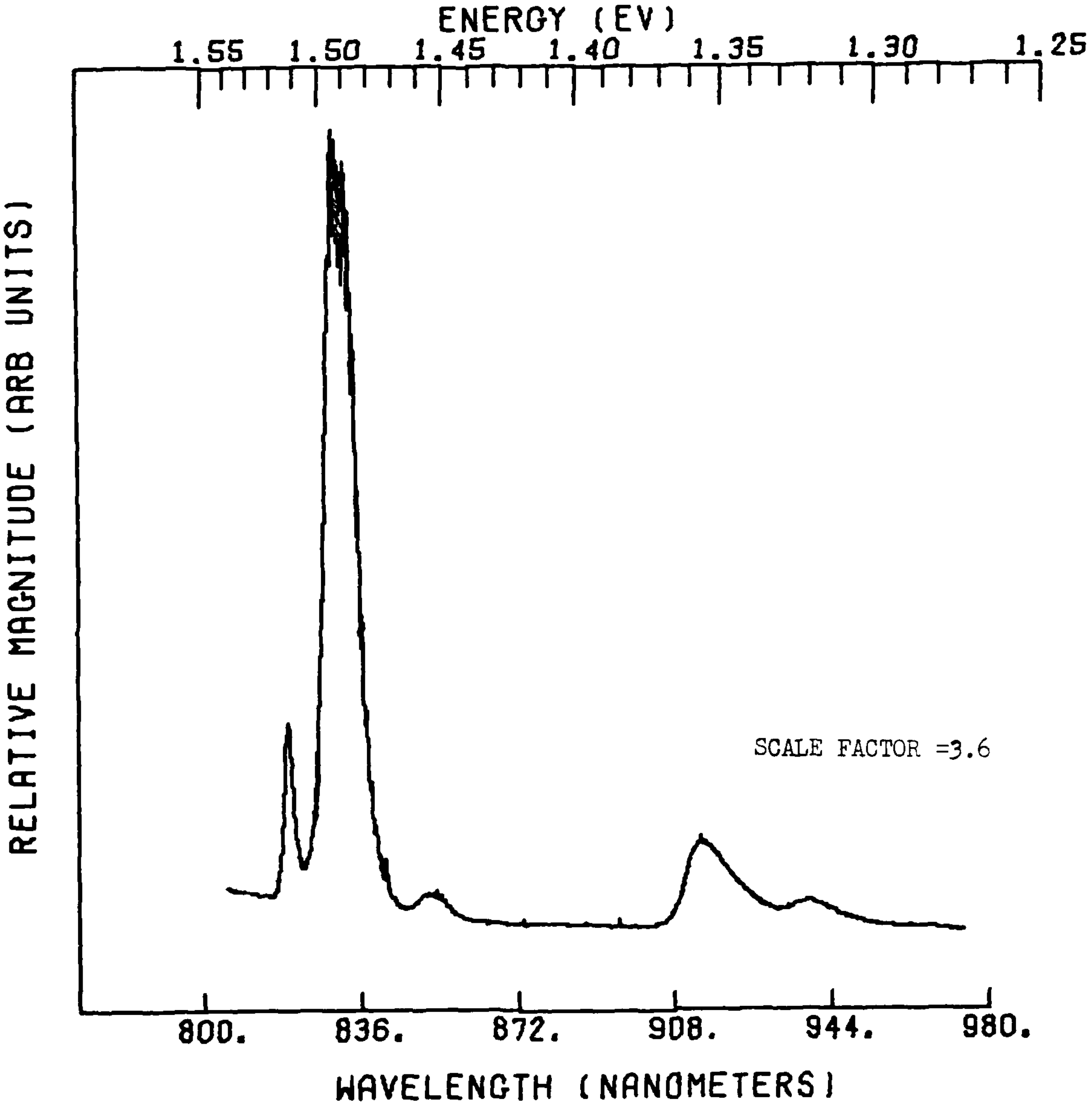

Figure 6. Photoluminescence of Sample CS4679/75 After Annealing with $Si_3N_4$ Cap in $H_2$ at 750°C for 20 Minutes

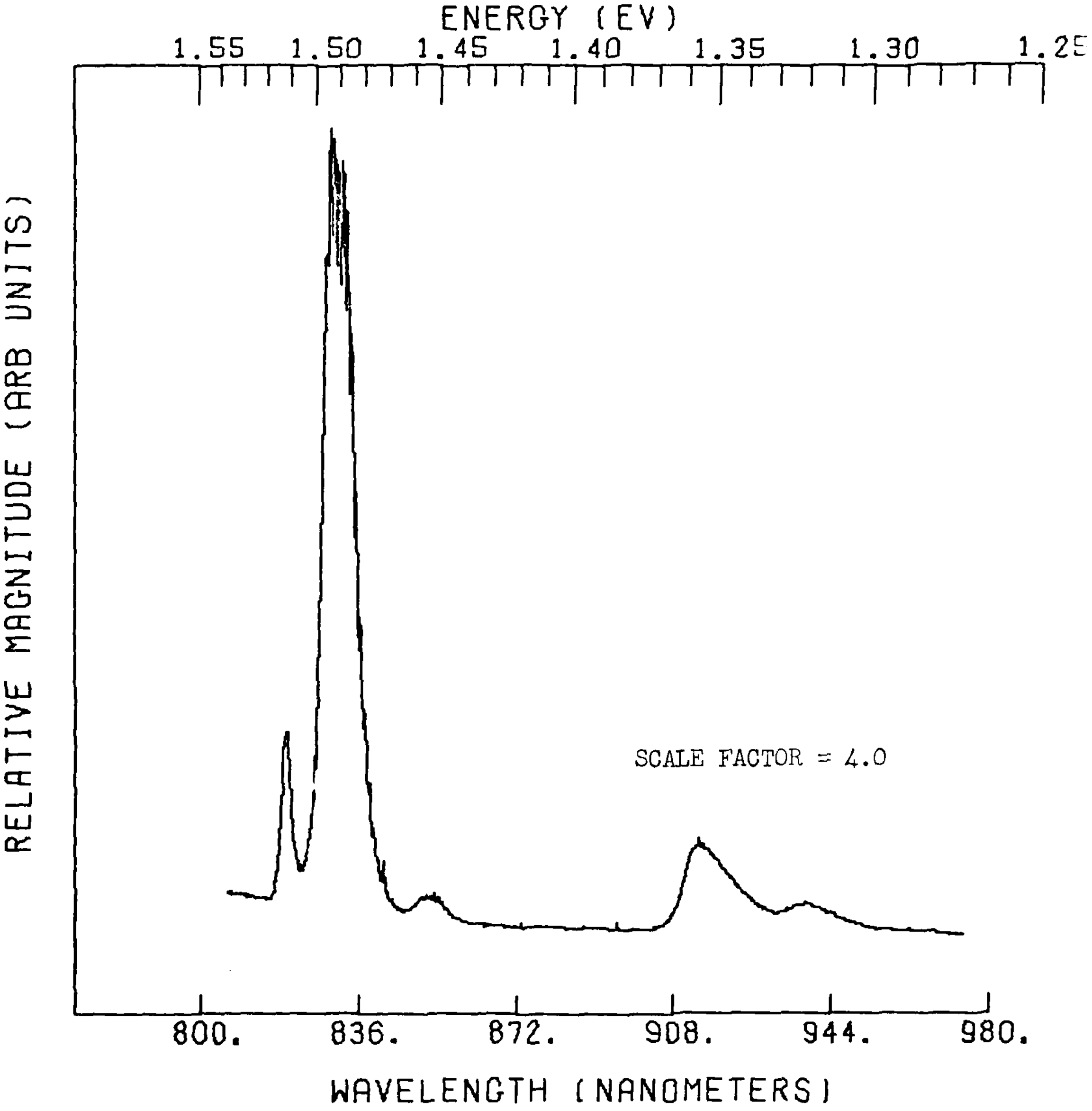

Figure 7. Photoluminescence of Sample CS4679/75 After Annealing with $Si_3N_4$ Cap in $H_2$ at 800°C for 20 Minutes.

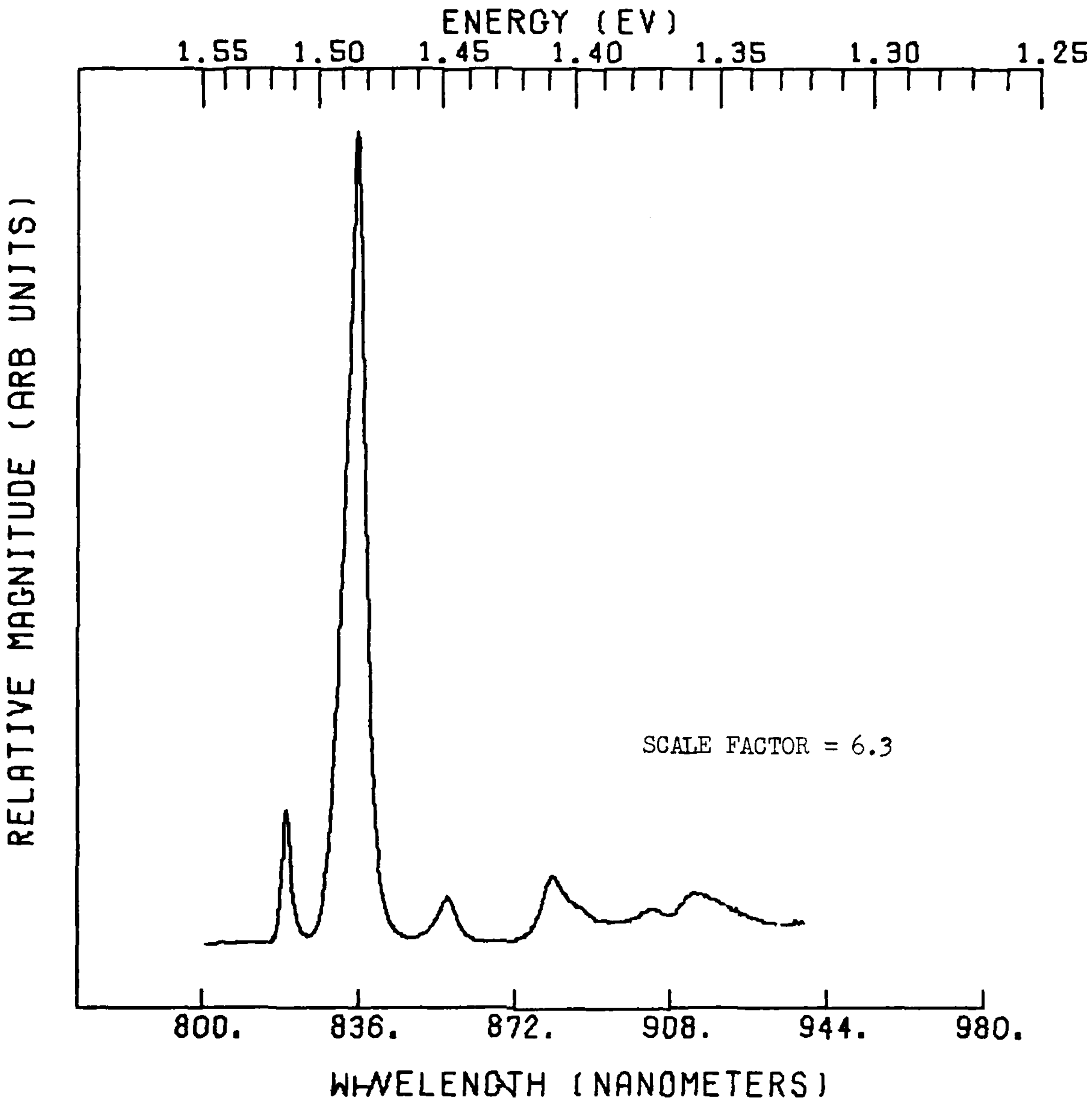

Figure 8. Photoluminescence of Sample CS4679/75 After Annealing with $Si_3N_4$ Cap in $H_2$ at 850°C for 20 Minutes.

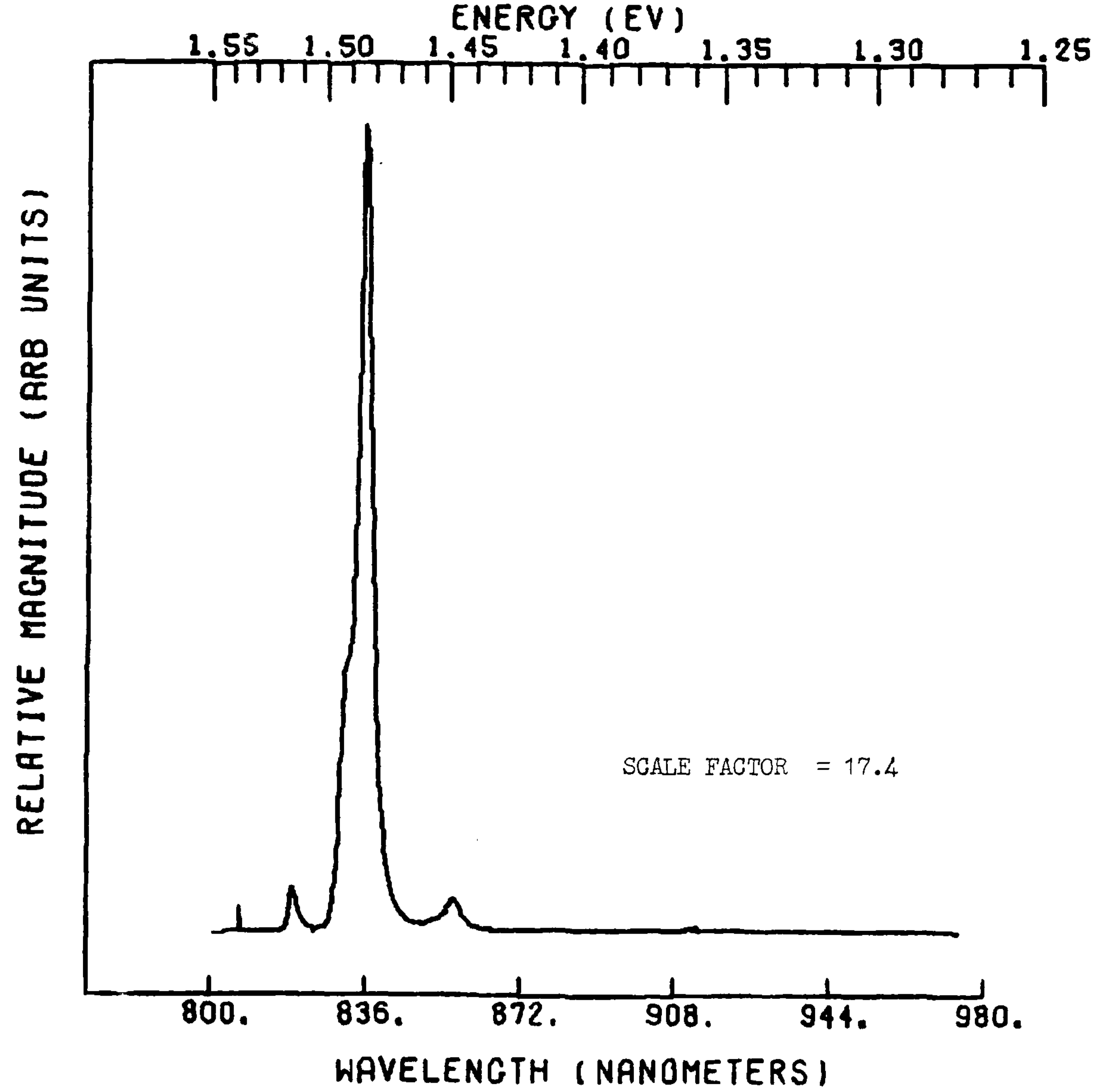

Figure 9. Photoluminescence of Sample CS4679/75 After Annealing with $Si_3N_4$ Cap in $H_2$ at 900°C for 20 Minutes.

Samples Annealed in Ar. Figure 10 shows the spectrum of one of the two Ar-annealed samples (the two spectra were identical). This shows the growth of the 1.489 eV Zn peak and the disappearance of the peak at 1.495 eV and its phonon replicas. Also evident is the reduction of the Cu acceptor -As vacancy peak, a predictable consequence of annealing. These samples did not convert to p-type, but showed a sharp decrease in resistivity, as can be seen in table 1.

A temperature study was performed on $Si_3N_4$ capped samples annealed in Ar in the same way as was done for $H_2$ annealed samples. Figures 11-14 show the resultant spectra. These show the emergence and growth with increasing temperature of the 1.41 eV peaks, but without the Si peak which appeared in the $H_2$-annealed samples. As with the $H_2$-annealed samples, conversion to p-type did not take place, but resistivity decreased sharply.

Samples Annealed in $N_2$. Figure 15 shows the spectrum of one of the two $N_2$ annealed samples. This spectrum is virtually the same as the spectrum for the $H_2$-annealed sample in that both the 1.485 eV Si peak and the 1.408 eV peak are present, although, when compared to the exciton peak, neither is as large as in the $H_2$-annealed samples. These two samples did not convert to p-type; further, they were the only samples in this study which maintained a high

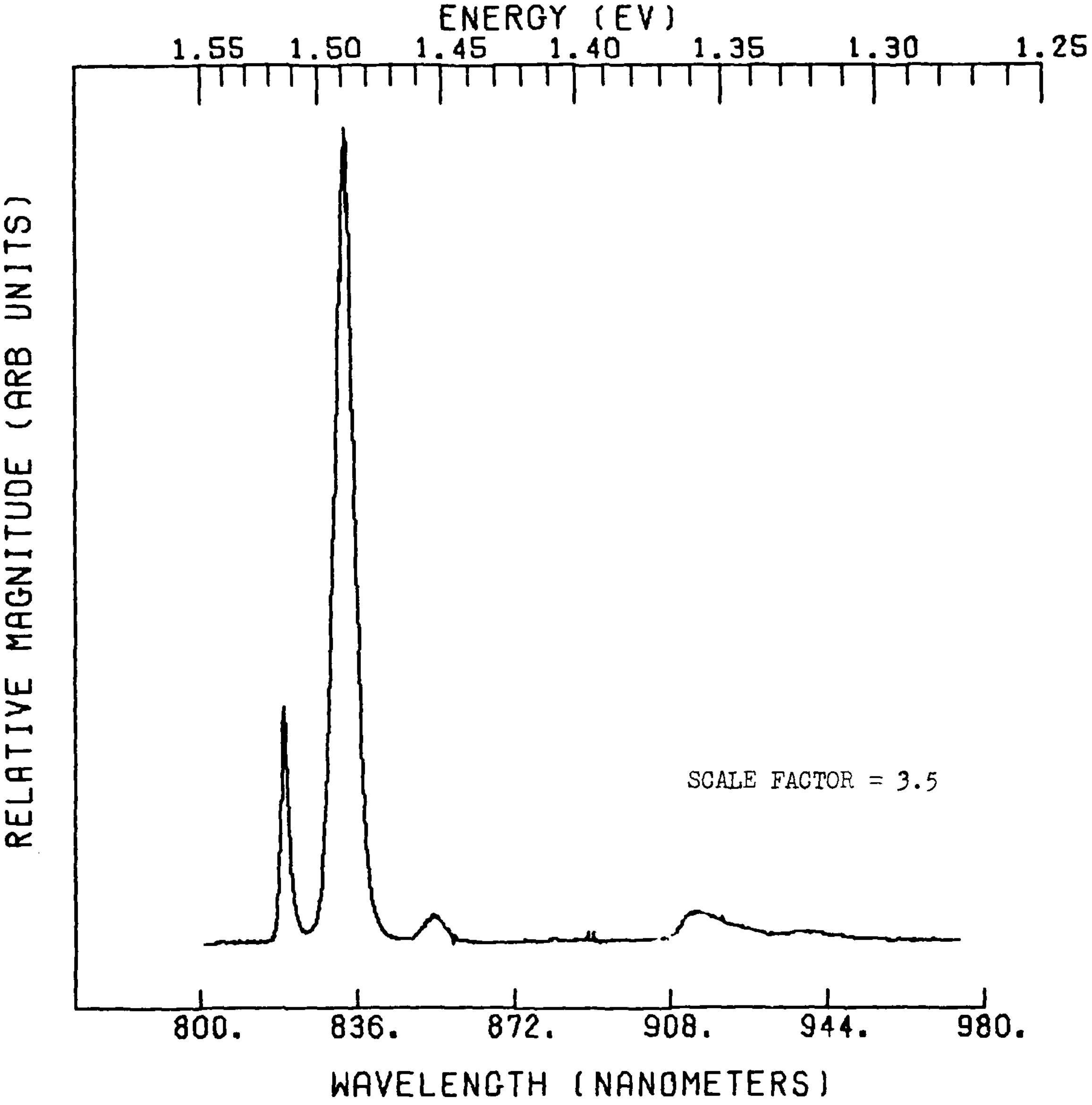

Figure 10. Photoluminescence of Sample CS4679/75 After Annealing in Ar at 850°C for 20 Minutes.

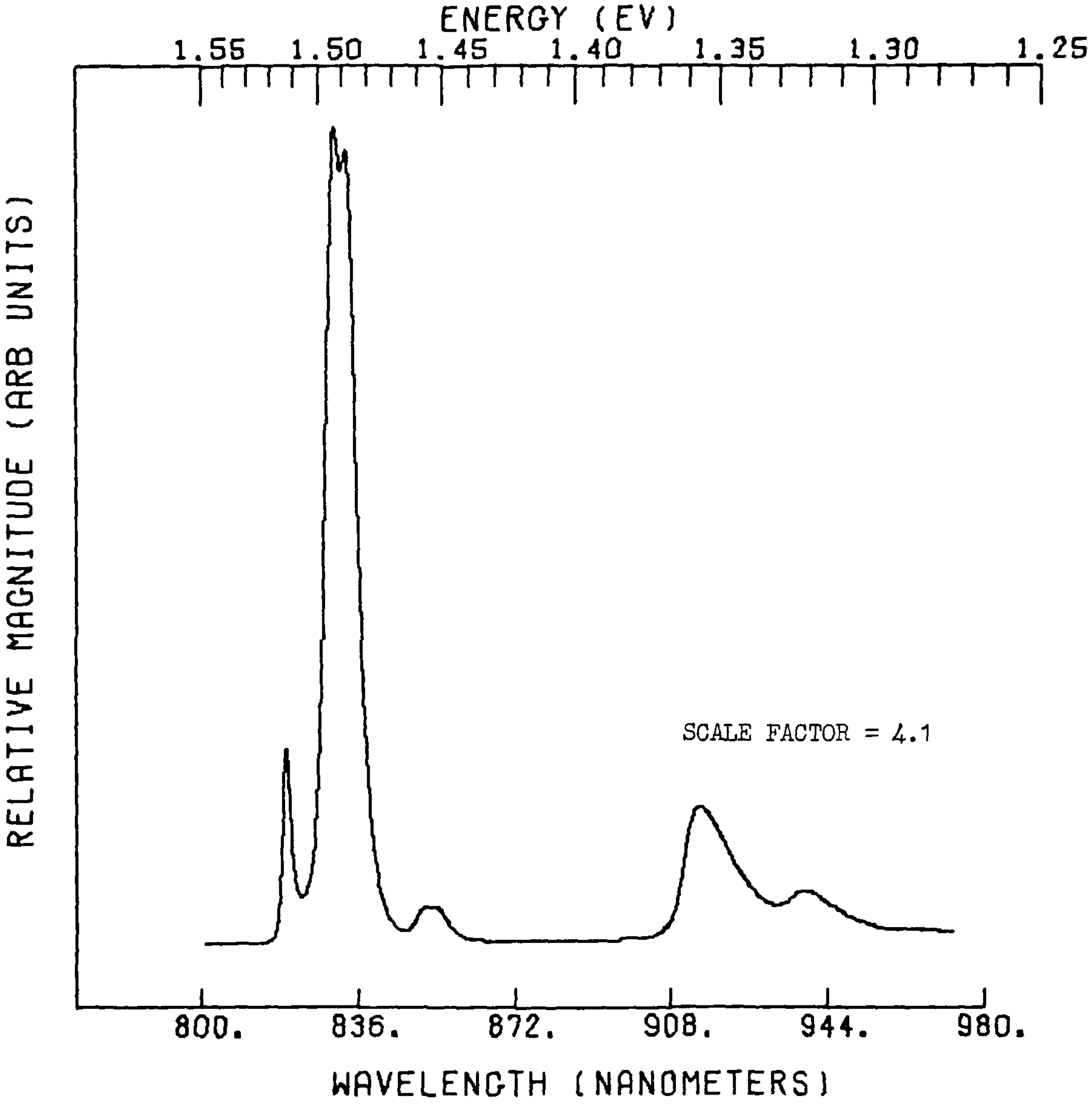

Figure 11. Photoluminescence of Sample CS4679/75 After Annealing with $Si_3N_4$ Cap in Ar at 750°C for 20 Minutes.

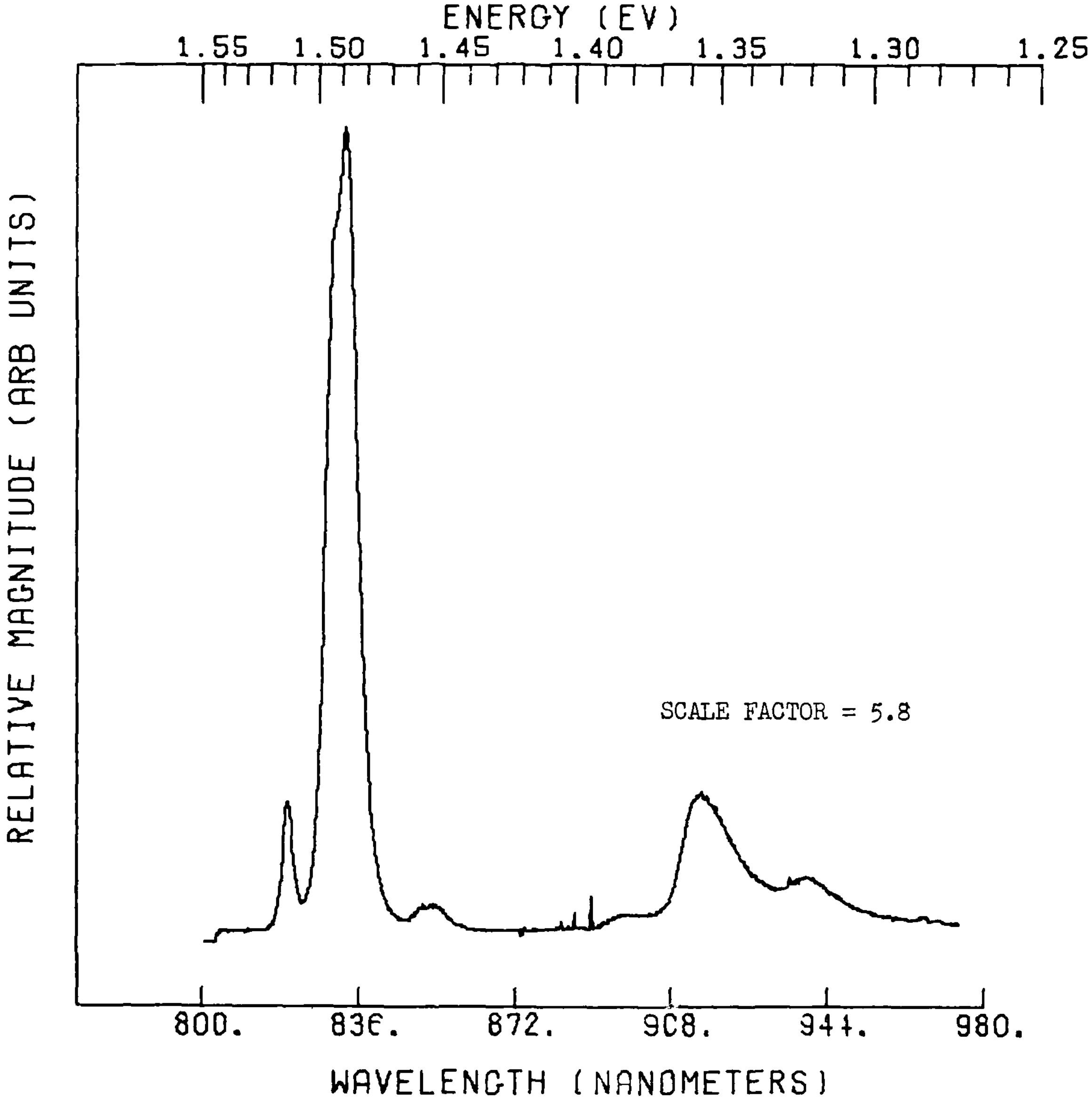

Figure 12. Photoluminescence of Sample CS4679/75 After Annealing with $Si_3N_4$ Cap in Ar 800°C for 20 Minutes.

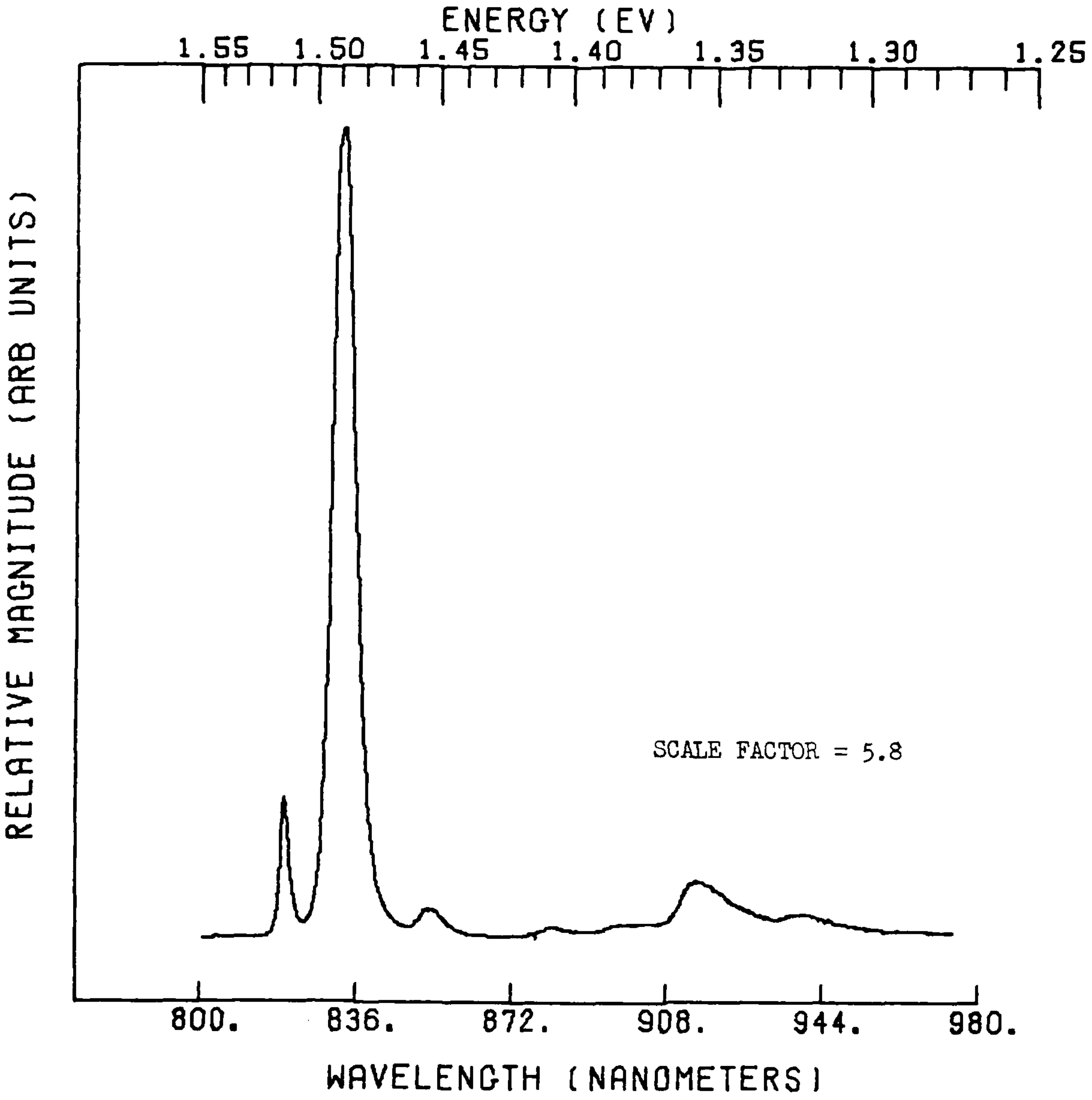

Figure 13. Photoluminescence of Sample CS4679/75 After Annealing with $Si_3N_4$ Cap in Ar 850°C for 20 Minutes.

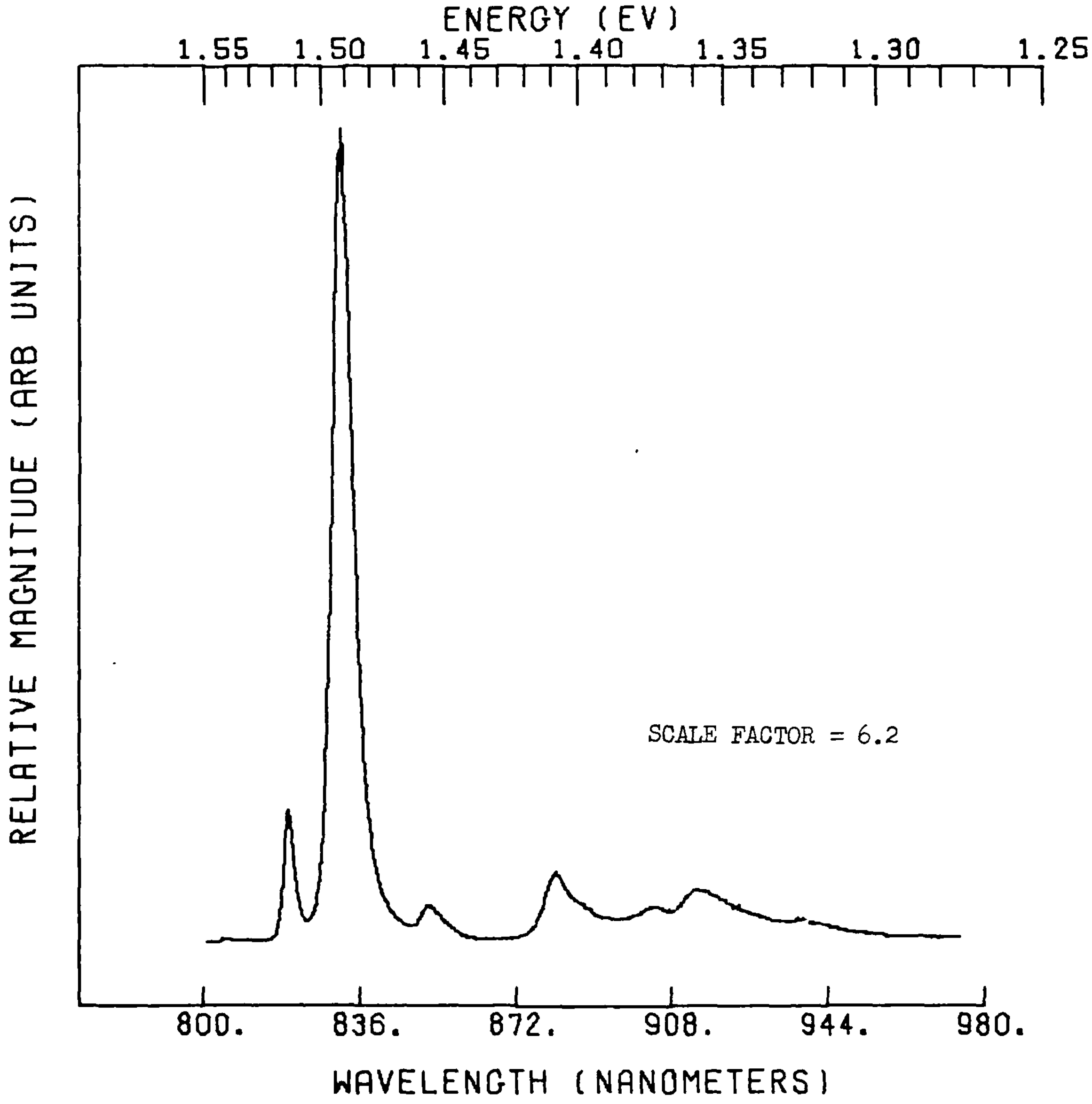

Figure 14. Photoluminescence of Sample CS4679/75 After Annealing with $Si_3N_4$ Cap in Ar 900°C for 20 Minutes.

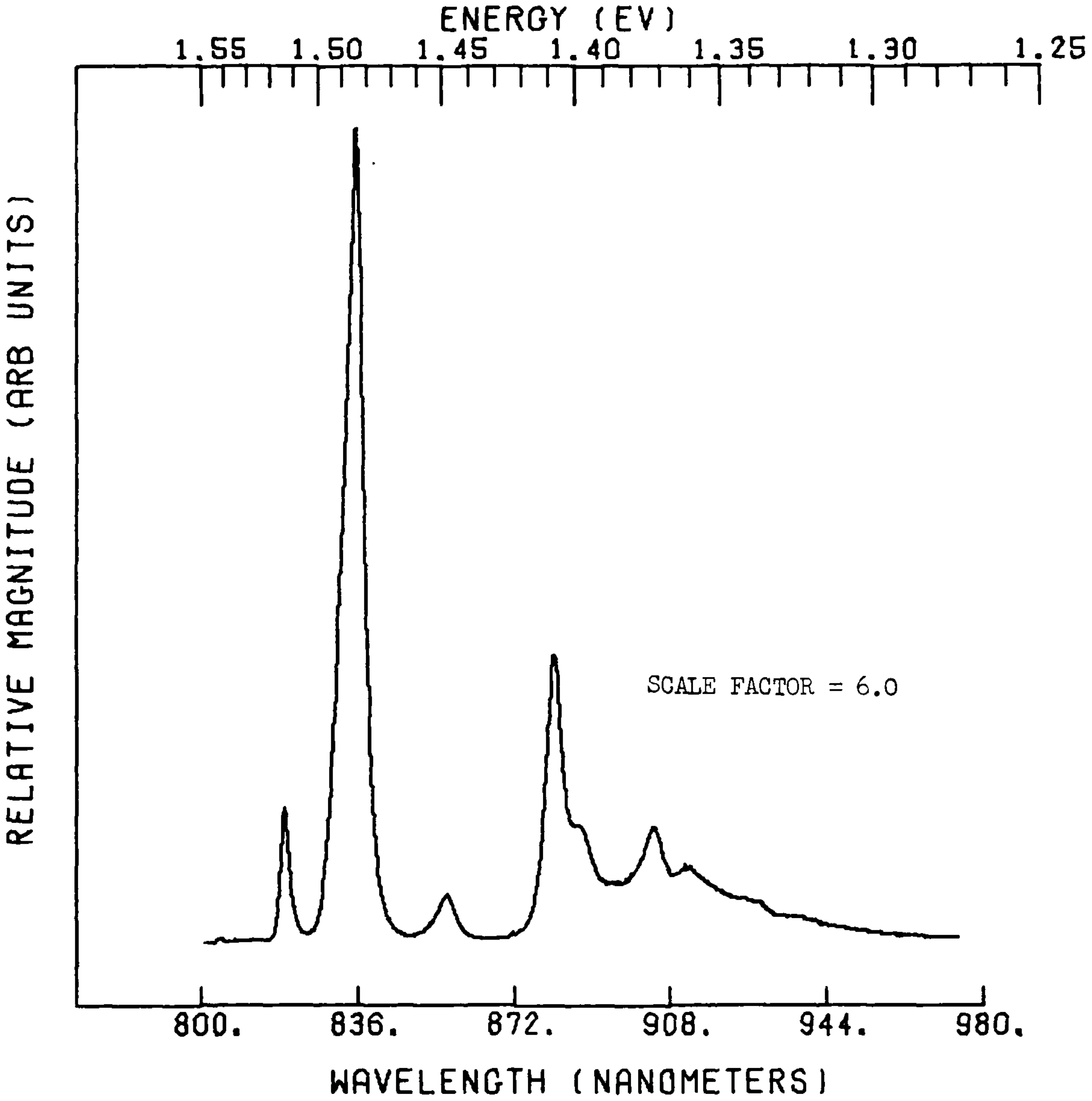

Figure 15. Photoluminescence of Sample CS4679/75 After Annealing in $N_2$ at 850°C for 20 Minutes.

degree of resistivity after annealing, as can be seen from table 1.

## Cr-doped GaAs with VPE Buffer Layer

Unannealed Sample. Figure 16 shows the spectrum of the epitaxial sample before annealing. In addition to the exciton peaks at 1.514 eV and the Cu acceptor-As vacancy peaks at 1.356 eV and 1.320 eV, three acceptor peaks are visible at 1.4941 eV, 1.4898 eV and 1.4870 eV. The 1.494 eV peak is, as before, attributed to a band-to-Si acceptor recombination. The other peaks are identified as a band-to-acceptor recombination at 1.490 eV and a donor-to-acceptor recombination at 1.487 eV involving a Zn acceptor (Ref 4:350).

Samples Annealed in $H_2$. Two epitaxial samples were annealed in $H_2$: one with a $Si_3N_4$ cap and one without. Figure 17 shows the spectrum of the uncapped sample. This spectrum shows two changes from the spectrum of the unannealed sample: the appearance of the 1.409 eV vacancy line and phonon replicas, and a pair of lines at 1.479 eV and 1.477 eV. The 1.479 eV line corresponds to the position reported by Ashen et al for a band-to-Ge acceptor recombination, and the 1.477 fits the theoretical position of a donor-to-Ge acceptor recombination. However, these lines also correspond to lines which, although they do not vary with Sn-doping concentration and are therefore believed to be caused

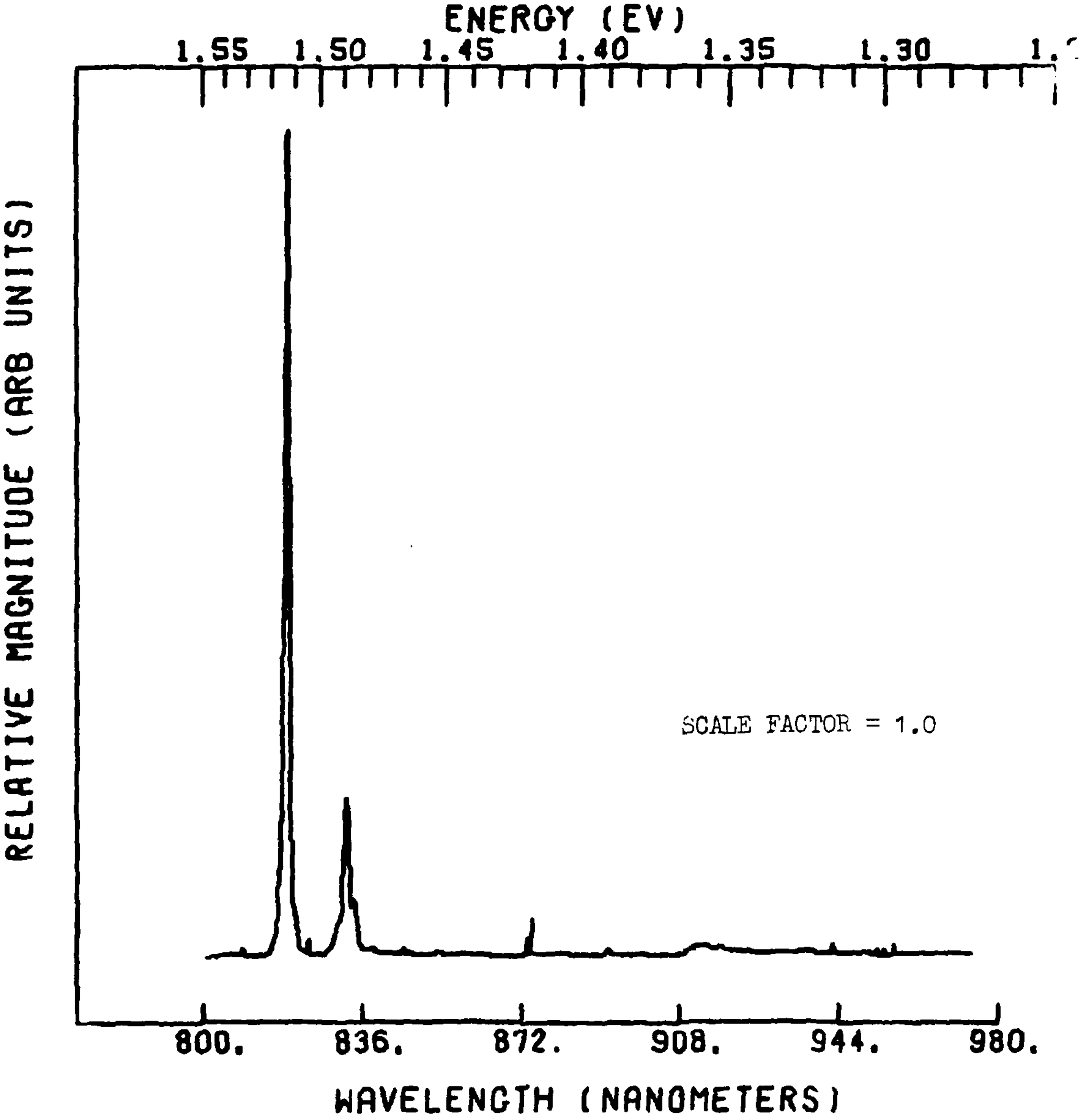

Figure 16. Photoluminescence of Sample CS4679/75 with VPE Buffer Layer Before Annealing

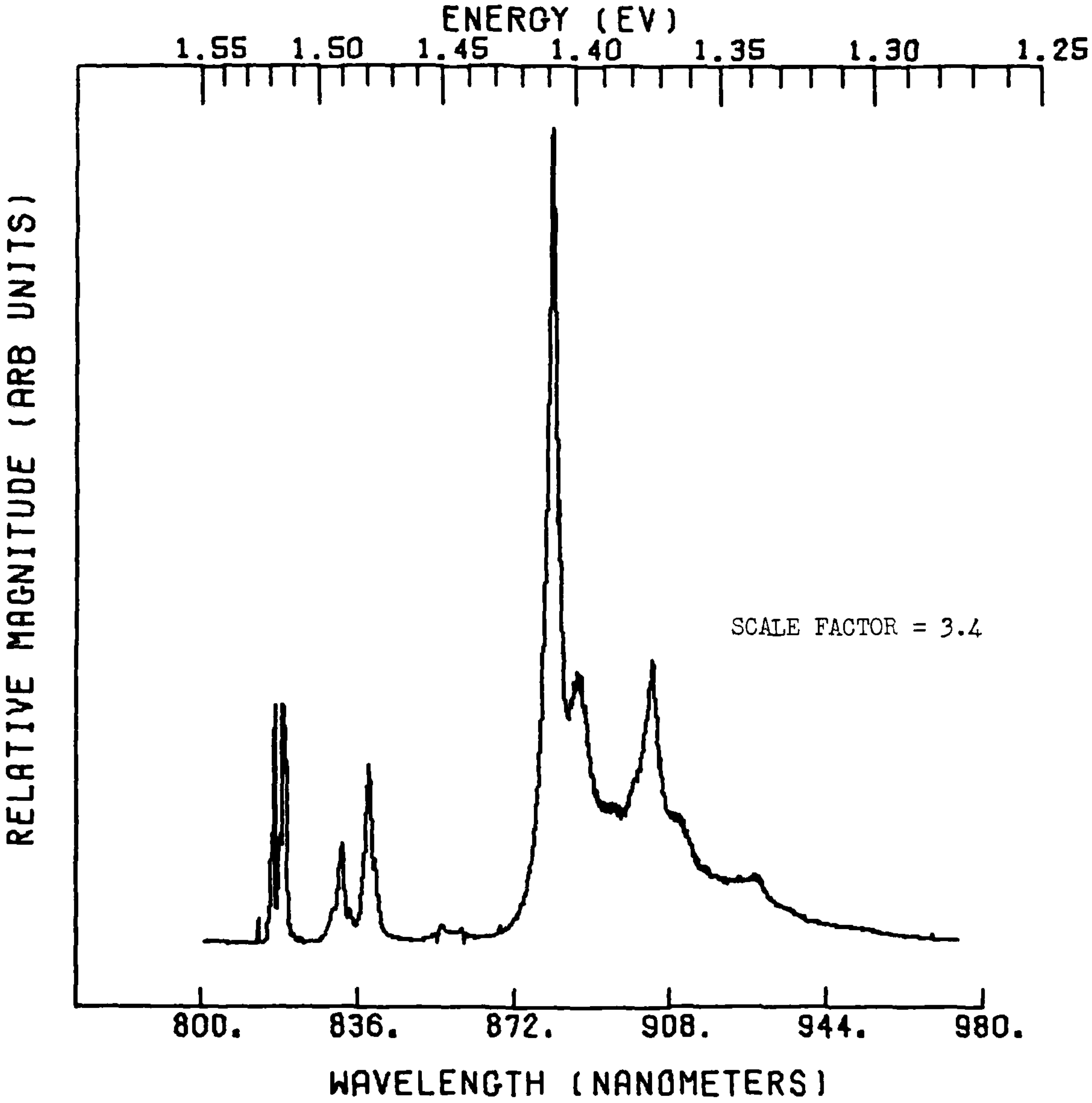

Figure 17. Photoluminescence of Sample CS4679/75 With VPE Buffer Layer After Annealing in $H_2$ at 850°C for 20 Minutes.

by other, unknown impurities, are found to be present in samples containing Sn impurities (Ref 4:386). These lines, then, whether or not they are caused by Ge, are believed to be present due to the Sn impurities which were introduced into the epitaxial growth system at AFWAL (See Sample Data section). These lines were present in all annealed epitaxial samples examined.

Figure 18 shows the spectrum of the $Si_3N_4$ encapsulated epitaxial sample after annealing in $H_2$. The lines at 1.479 eV and 1.477 eV are again present, but the C peak at 1.493 eV and the Cu peak at 1.356 eV have both grown considerably. The 1.41 eV peaks are not present. This sample converted to p-type, as did all of the epitaxial samples examined.

Samples Annealed in Ar. Figure 19 shows the spectrum of the epitaxial sample annealed under Ar without a cap. As the signal from this sample was extremely weak, it was necessary to use a spectrometer slit width of .7 mm, which accounts for the very poor resolution in this spectrum. This spectrum shows the 1.479 and 1.477 eV peaks which appeared in all epitaxial samples, plus the appearance of a peak at 1.483 eV, which was identified in other samples as Si.

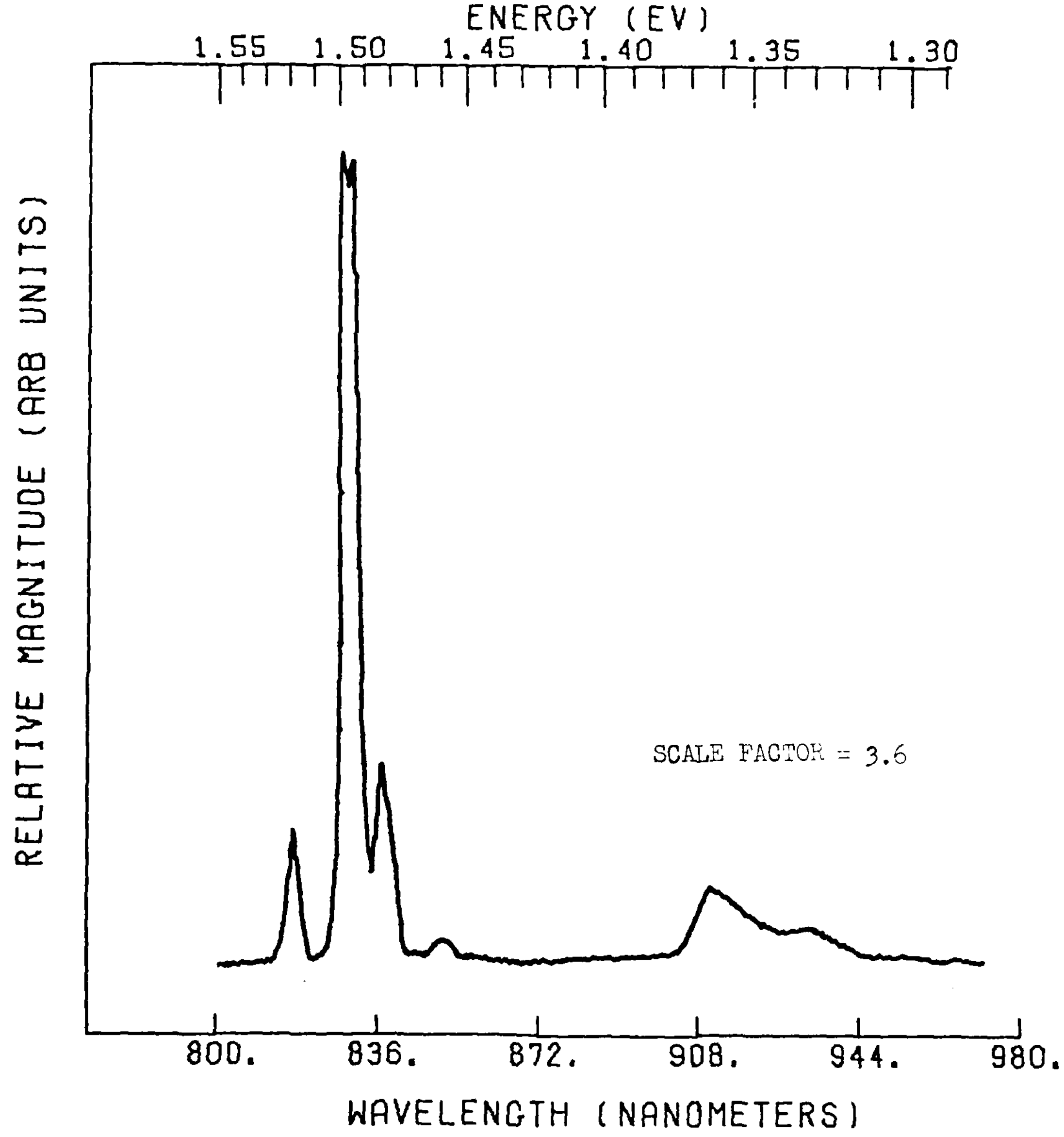

Figure 18. Photoluminescence of Sample CS4679/75 with VPE Buffer Layer and $Si_3N_4$ Cap After Annealing in $H_2$ at 850 °C for 20 Minutes.

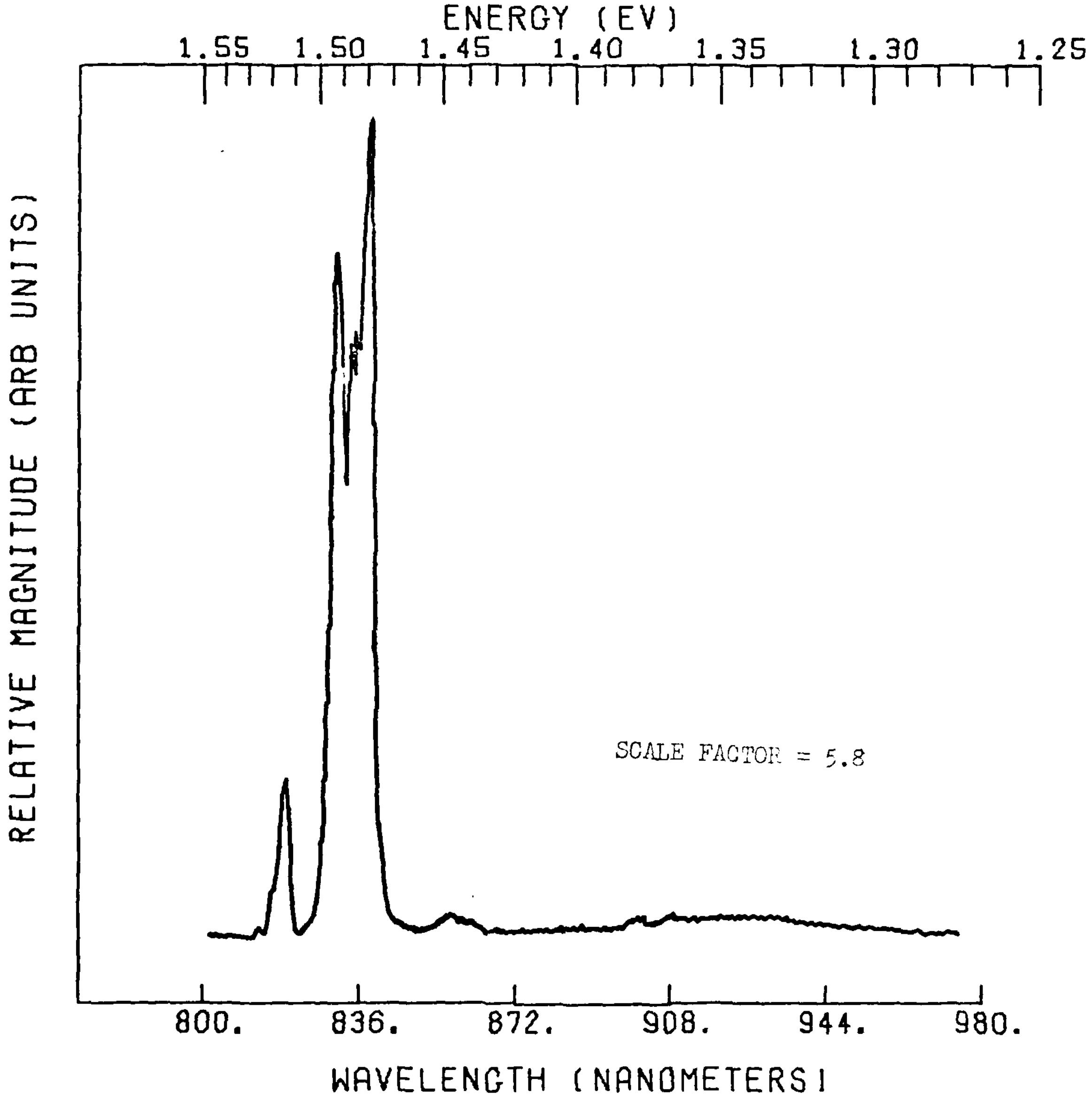

Figure 19. Photoluminescence of Sample CS4679/75 with VPE Buffer Layer After Annealing in Ar at 850°C for 20 Minutes.

Figure 20 shows the spectrum for the Ar-annealed, $Si_3N_4$ capped sample. Except for the smaller Cu peak, this spectrum is identical to that of the $H_2$-annealed, $Si_3N_4$ capped sample.

Samples Annealed in $N_2$. Figure 21 shows the spectrum of the $N_2$-annealed epitaxial sample. Except for the smaller 1.41 eV peaks, this spectrum is identical to that of the $H_2$-annealed epitaxial sample.

### Undoped Samples

Unannealed Samples. Figure 22 shows the spectrum of sample W8/20 before annealing. Other than the exciton line, only two peaks are visible: the Zn band-to-acceptor line at 1.488 eV and its phonon replica at 1.452 eV.

Figures 23 and 24 show the spectrum of sample WBN6/24. Five lines can be seen in the acceptor peak: The carbon line at 1.494 eV, two lines at 1.490 eV and 1.485 eV which are believed to be band-acceptor and donor-acceptor recombinations involving Cd, and two lines at 1.492 eV and 1.487 eV which are believed to be band-acceptor and donor-acceptor transitions involving Zn (Ref 4:350, Ref 15:1051).

Samples Annealed in $H_2$. The spectrum of sample W8/20 is shown in figure 25. This spectrum shows two changes over the unannealed spectrum: The appearance of a shoulder on

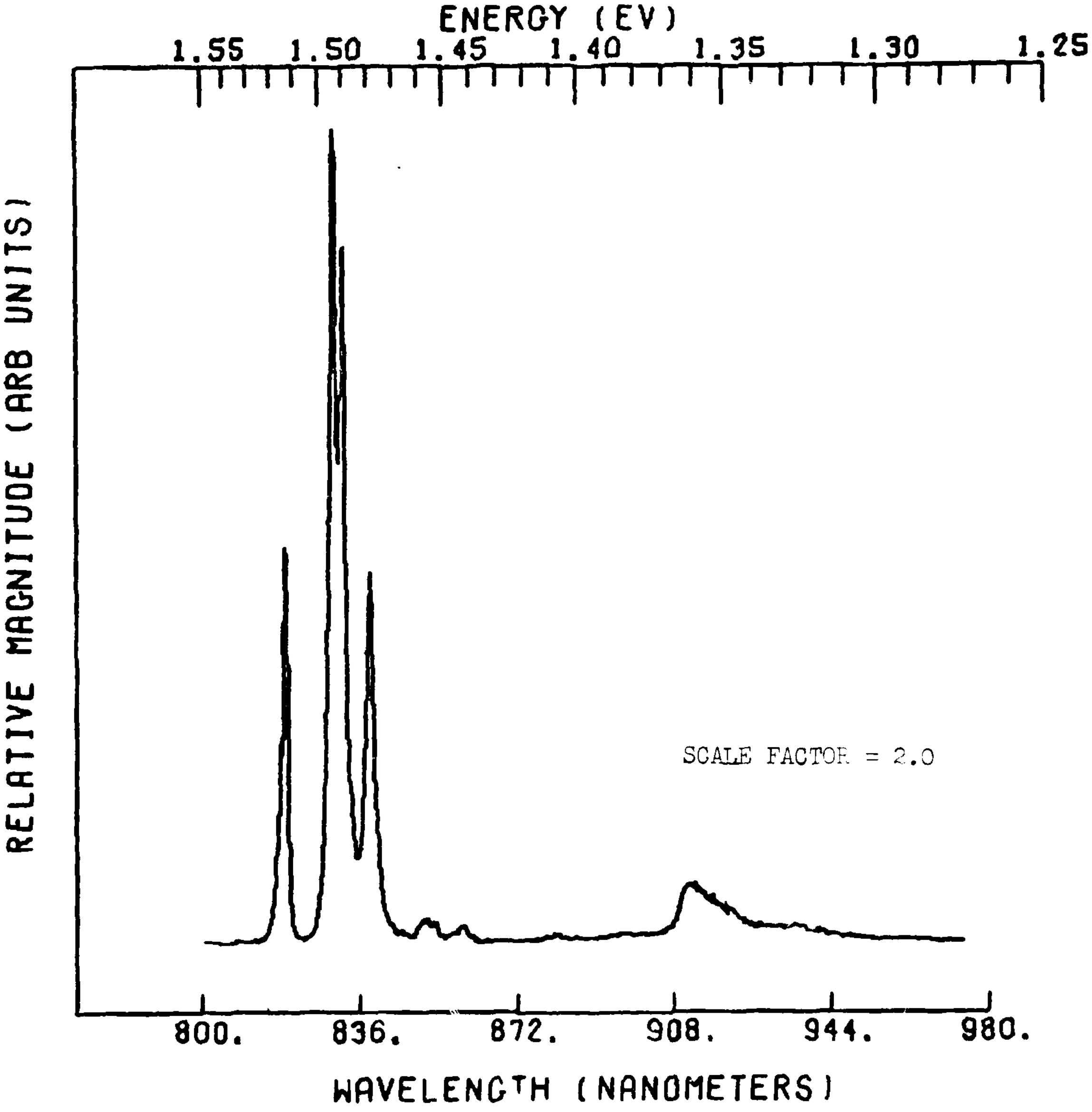

Figure 20. Photoluminescence of Sample CS4679/75 with VPE Buffer Layer and $Si_3N_4$ Cap After Annealing in Ar at 850°C for 20 Minutes.

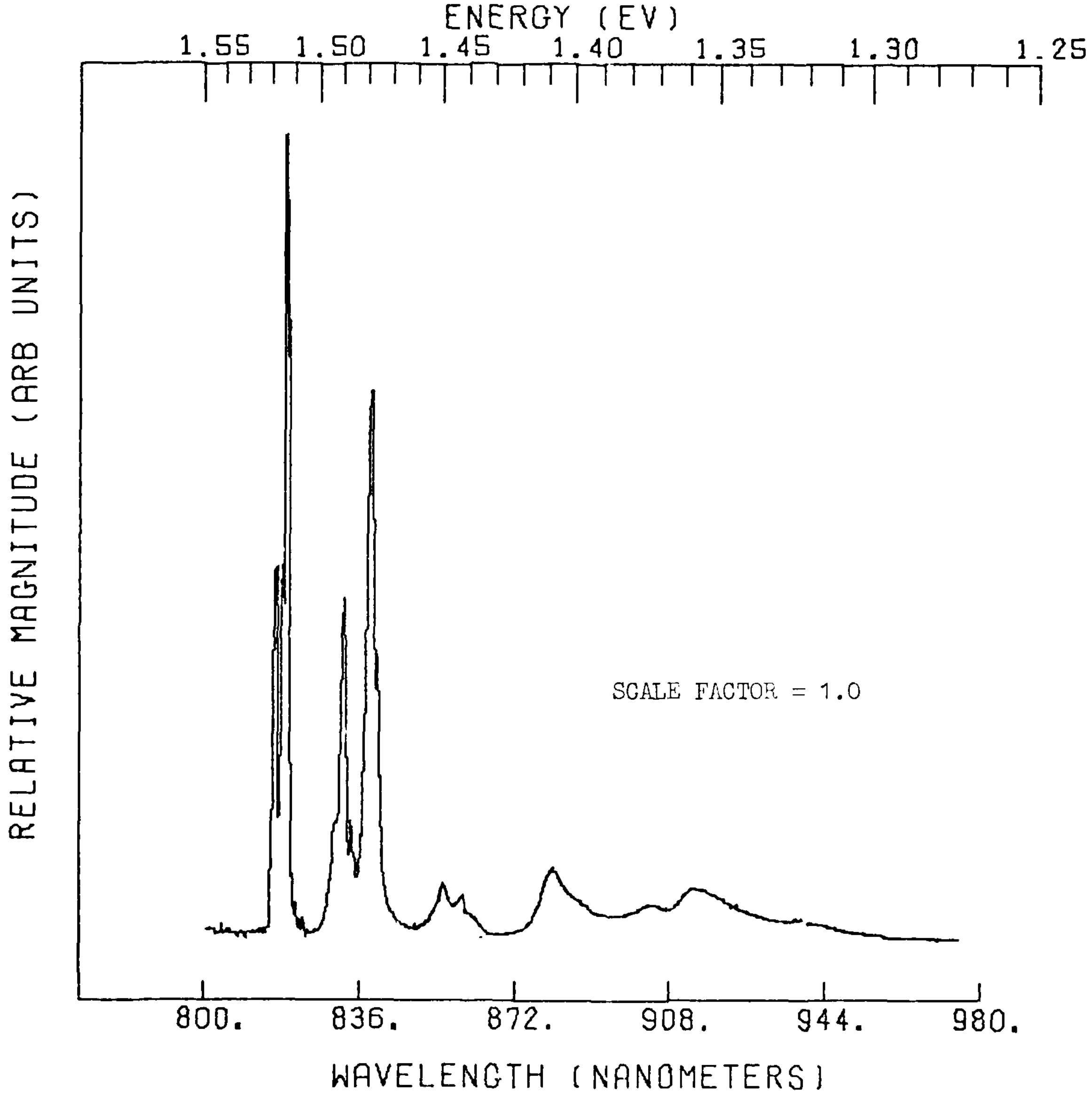

Figure 21. Photoluminescence of Sample CS4679/75 with VPE Buffer Layer After Annealing in $N_2$ at 850°C for 20 Minutes.

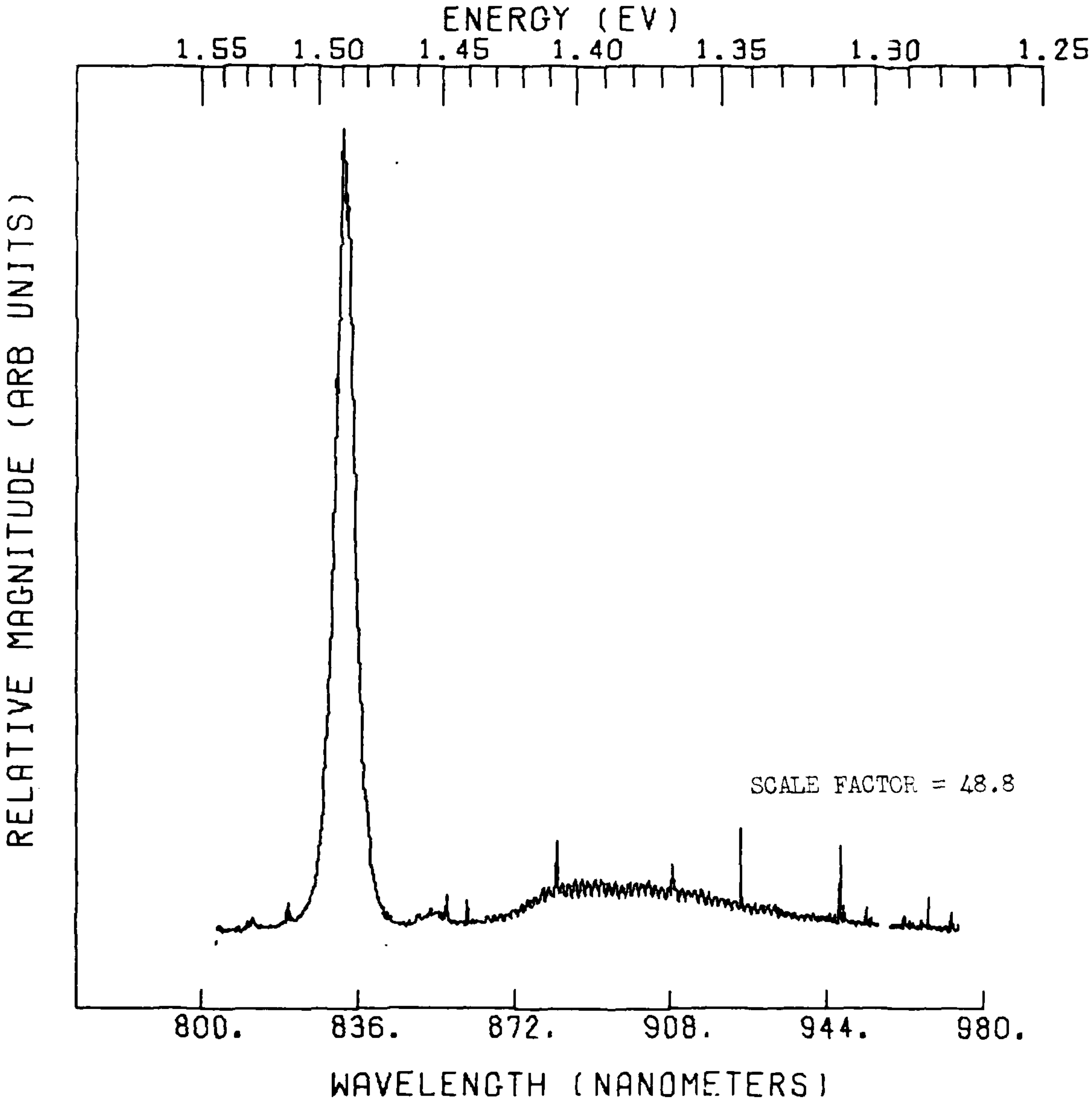

Figure 22. Photoluminescence of Sample W8/20 Before Annealing.

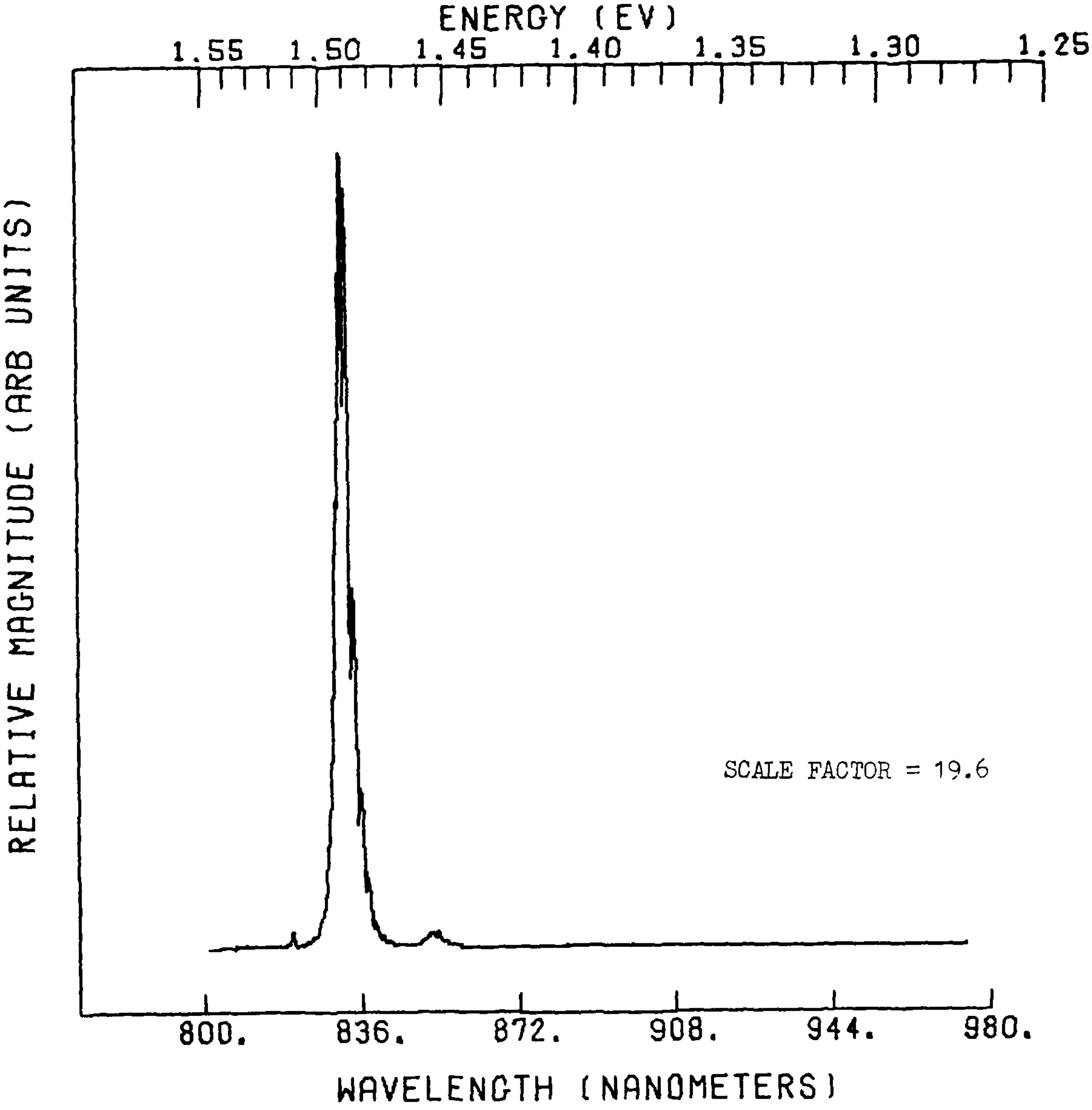

Figure 23. Photoluminescence of Sample WBN6/24 Before Annealing.

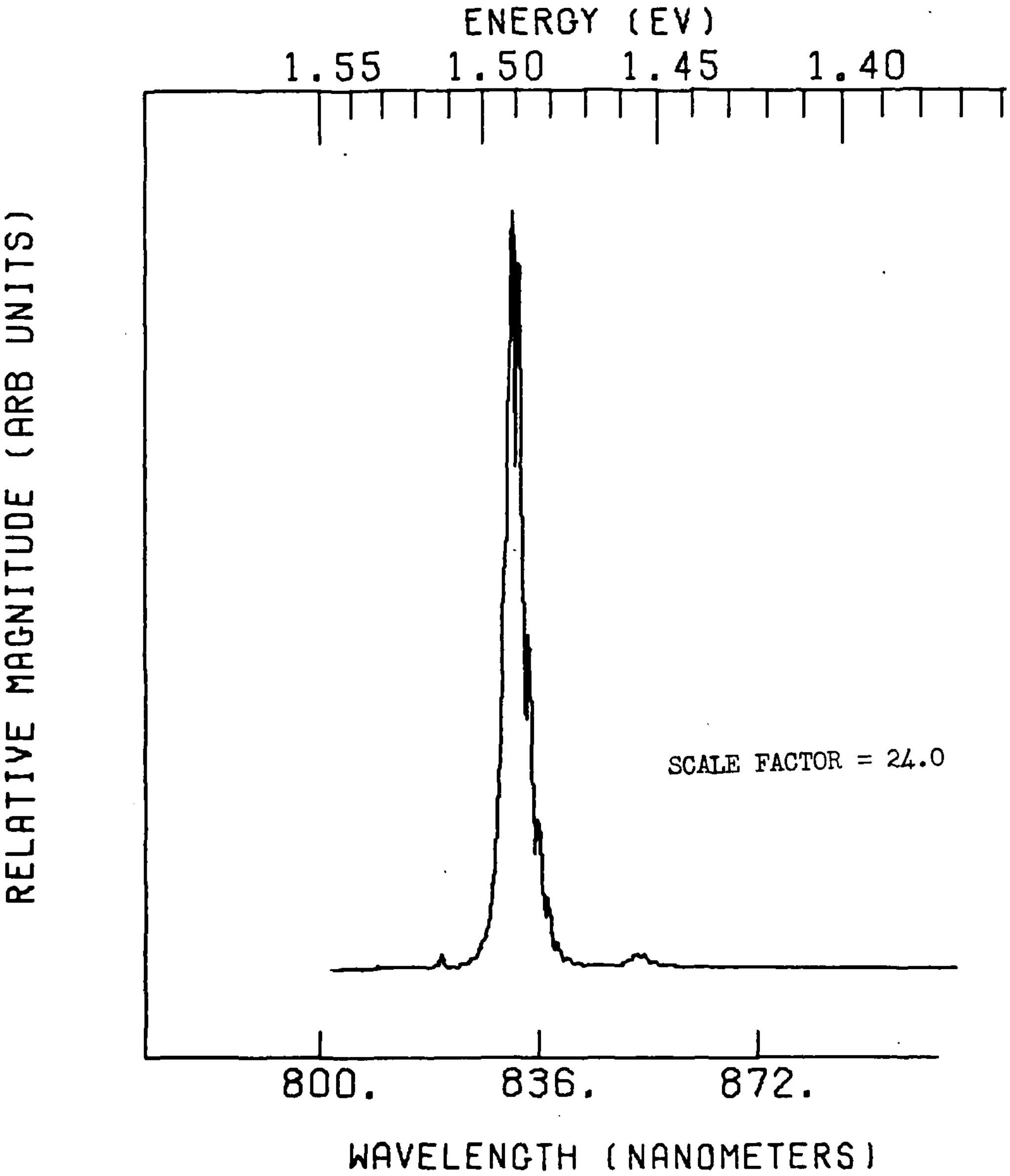

Figure 24. Photoluminescence Below 890nm of Sample WBN6/24 Before Annealing.

the acceptor peak at 1.493 eV, and the appearance of the lines at 1.408 eV. The 1.493 eV line is again identified as a C acceptor.

Figures 26 and 27 show the spectrum of sample WBN6/24. This spectrum also shows the 1.493 eV C-peak, but no evidence of Mn can be detected. Both samples W8/20 and WBN6/24 converted to p-type and exhibited very similar resistivities, as can be seen from table 1.

Samples Annealed in Ar. Both undoped, Ar annealed samples included a $Si_3N_4$ cap. Figure 28 shows the spectrum for sample W8/20. No difference can be detected between this spectrum and the unannealed spectrum. This sample did not convert to p-type, but exhibited mixed conductivity.

Figure 29 shows the spectrum for sample WBN6/24, which did convert to p-type. The only change in the spectrum of this sample is an increase in the height of the C-line at 1.494 eV.

## Comparison of Results

Table 2 shows the general results for samples annealed at 850°C. Resistivities are given to the nearest order of magnitude. Samples for which results were nearly identical are grouped together and the samples annealed at 750, 800, and 900°C are not included as their results are consistent with the 850°C results. Peaks noted in table 2 are those

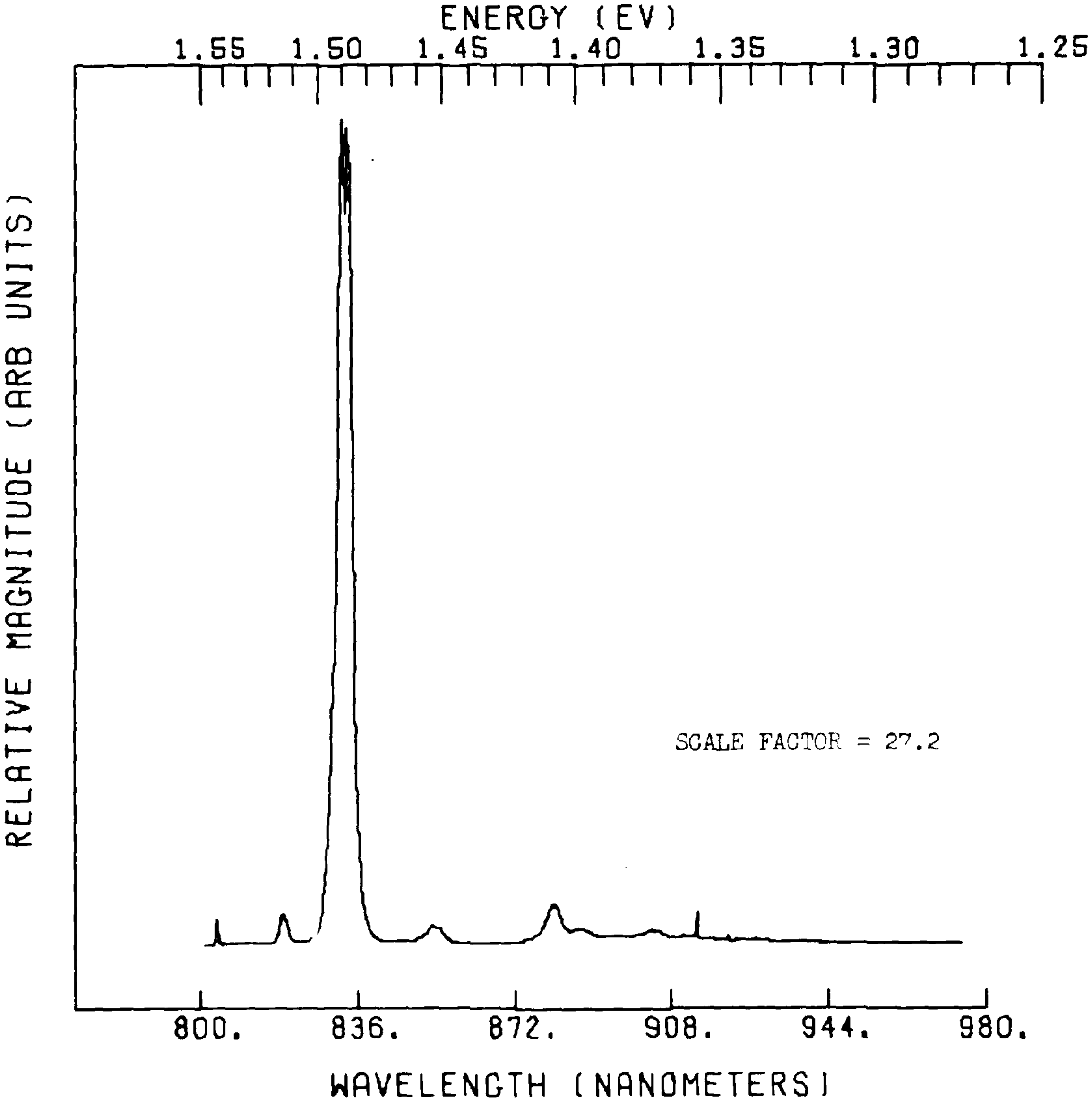

Figure 25. Photoluminescence of Sample W8/20 After Annealing in $H_2$ at 850°C for 20 Minutes.

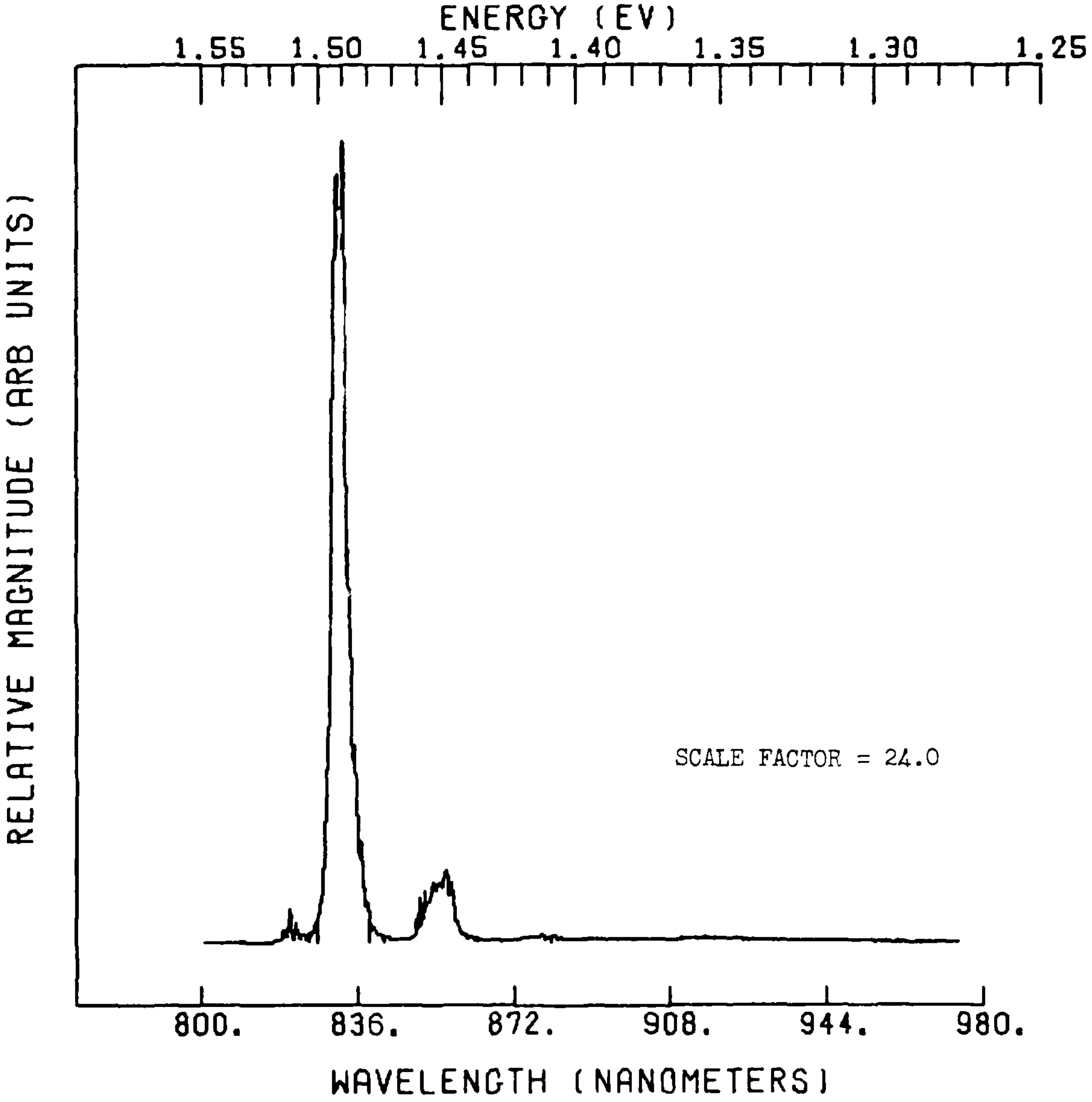

Figure 26. Photoluminescence of Sample WBN6/24 After Annealing in $H_2$ at 850°C for 20 Minutes.

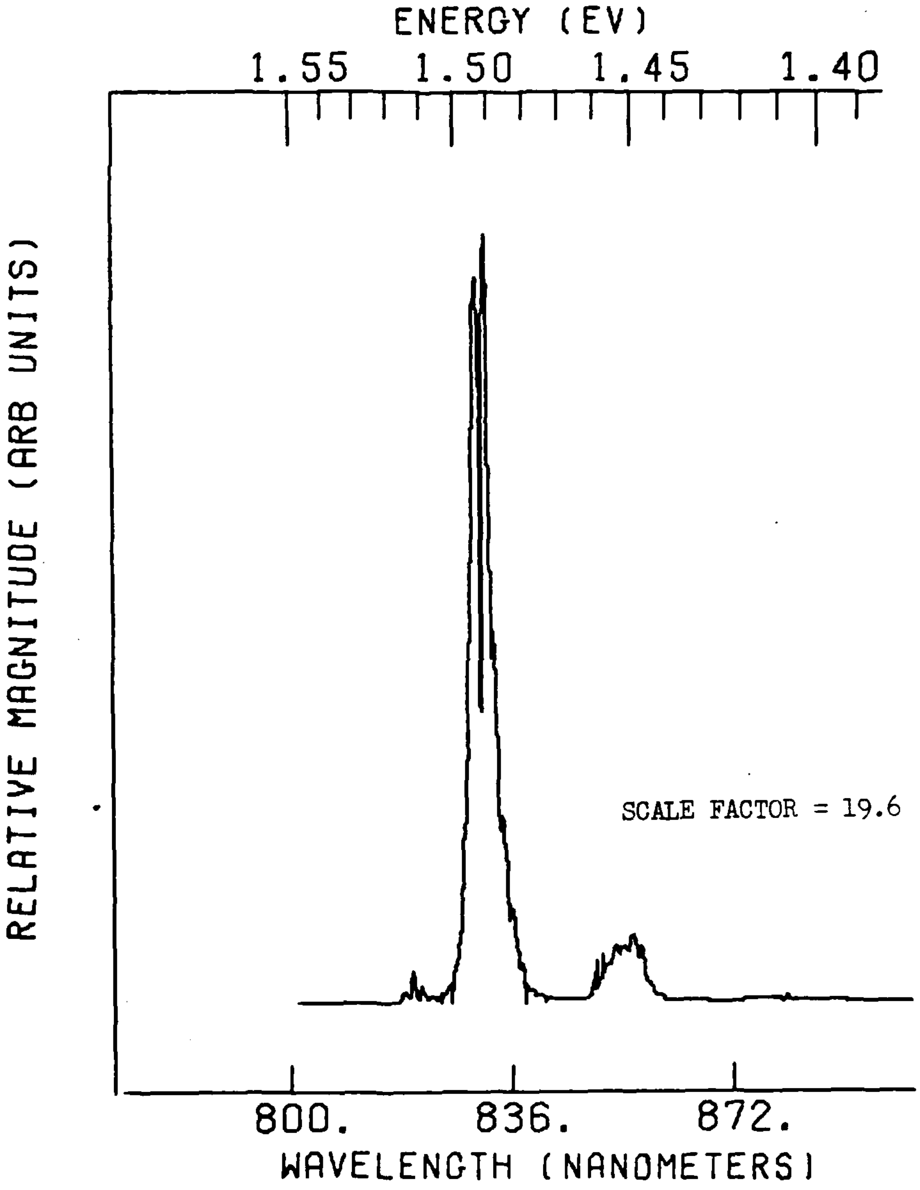

Figure 27. Photoluminescence Below 890NM of Sample WBN6/24 After Annealing in $H_2$ at 850°C for 20 Minutes.

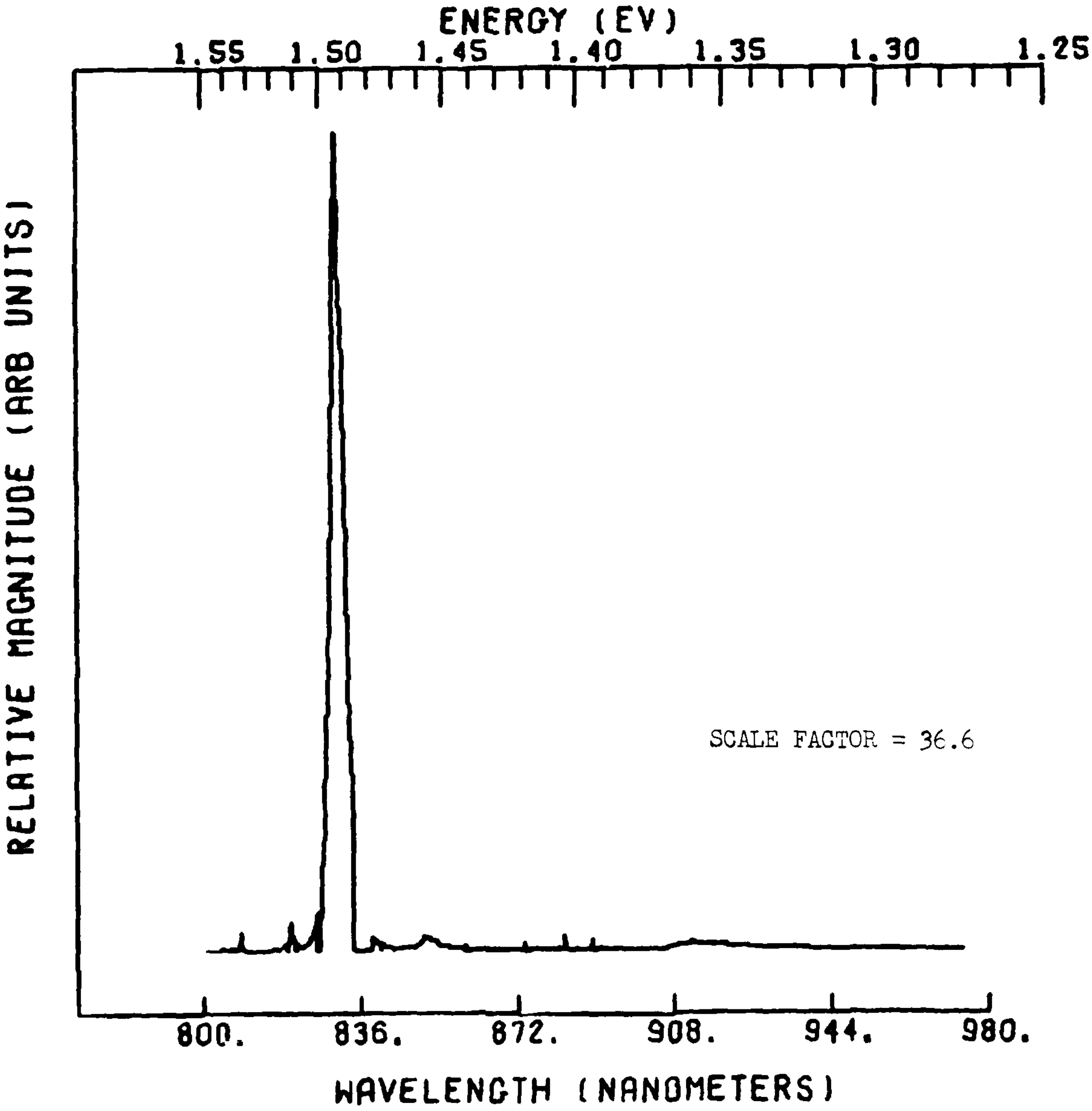

Figure 28. Photoluminescence of Sample W8/20 After Annealing with $Si_3N_4$ Cap in Ar at 850°C for 20 Minutes.

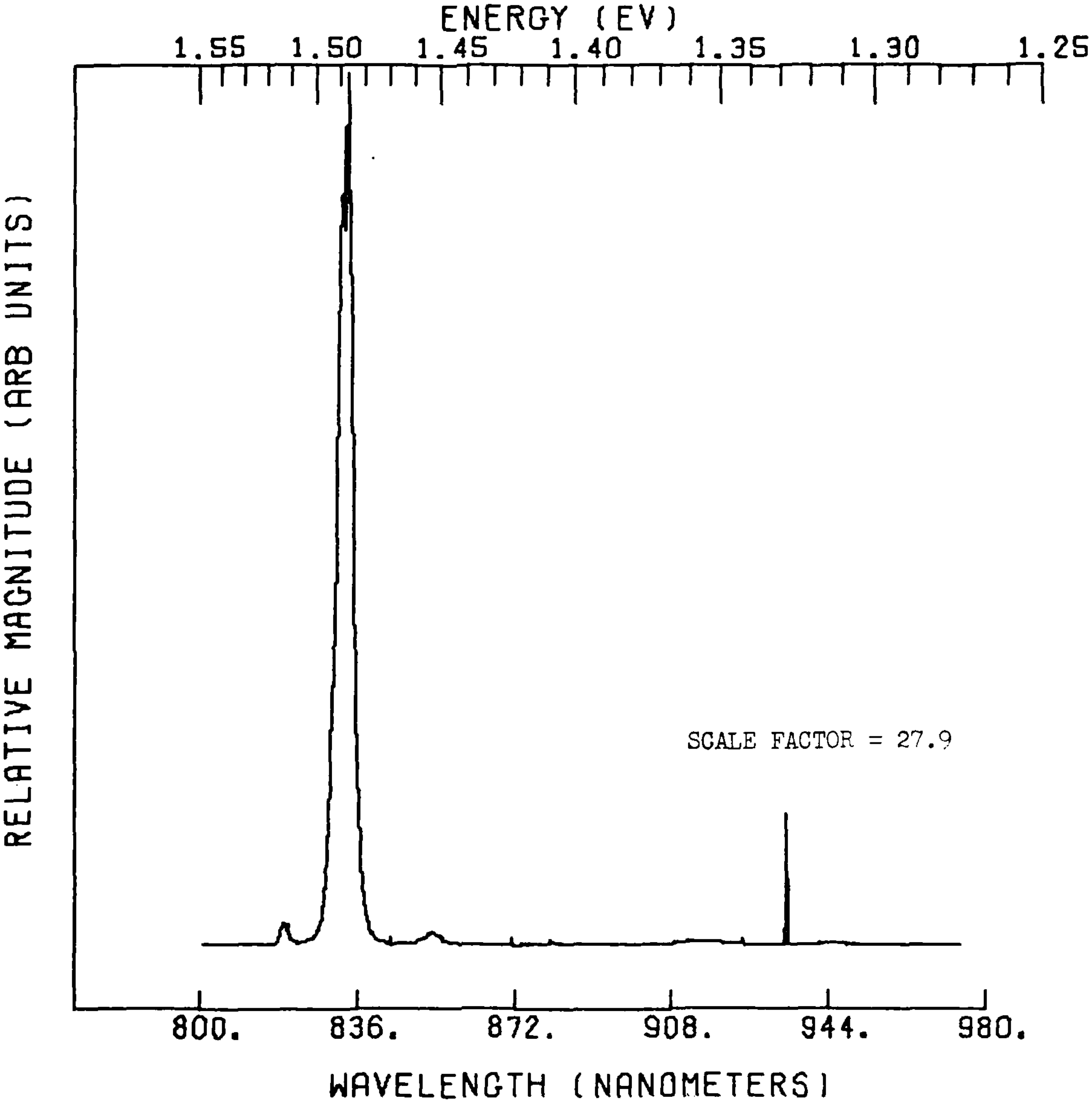

Figure 29. Photoluminescence of Sample WBN6/24 After Annealing with $Si_3N_4$ Cap in Ar at 850°C for 20 Minutes.

which either appeared or grew larger after annealing. For more exact data for individual samples, see the preceding discussion of results and table 1.

In the epitaxial samples, all converted to p-type and all showed the two lines at 1.48 eV, which were the only changes in spectrum common to all epitaxial samples. Although most previous studies of the thermal conversion problem have used epitaxial samples, none of them have reported these lines. Since lines at this position are found in GaAs with any amount of Sn dopant (Ref 4:386), it seems reasonable to conclude that these lines are caused by the Sn which was unfortunately introduced to the epitaxial-growth system at AFWAL. It also seems quite possible that the thermal conversion of these samples may have been caused by either Sn or the unknown impurity associated with it or by both. While this makes the usefulness of comparing the spectra of these samples with those of other samples studied quite limited, it does point out the possibility that thermal conversion can be caused by any of a variety of causes. This would indicate that trying to identify one impurity or combination of impurities as the cause of thermal conversion (as has been done in previous studies) may well be the wrong approach.

It seems evident from the large 1.41 eV lines in the $N_2$-annealed, non epitaxial samples that Mn is not responsible

# TABLE II

## SPECTRAL AND ELECTRICAL RESULTS

| Samples | $Si_3N_4$ Cap | Atmosphere | $\rho$ | Conversion | Peaks Observed |
|---|---|---|---|---|---|
| Undoped WBN6/24 $\rho=10^8$ |  | $H_2$ | $10^4$ | X | C |
|  | X | Ar | $10^5$ | X | C, Cu |
| Undoped W8/20 $\rho=10^8$ |  | $H_2$ | $10^4$ | X | Mn,C |
|  | X | Ar | $10^6$ |  |  |
| Cr-Doped Samples $\rho=10^{10}$ |  | $H_2$ | $10^4$ | X | Mn,Si |
|  |  | Ar | $10^4$ |  | Zn |
|  |  | $N_2$ | $10^8$ |  | Mn,Si |
|  | X | $H_2$ | $10^5$ |  | Mn,Si |
|  | X | Ar | $10^4$ |  | Mn,Si |
| Epitaxial Samples $\rho=10^8$ | X | $H_2$ | $10^4$ | X | C,Cu, 1.48eV |
|  | X | Ar | $10^6$ | X | C,Cu, 1.48eV |
|  |  | $N_2$ | $10^5$ | X | Mn, 1.48eV |
|  |  | $H_2$ | $10^4$ | X | Si, 1.48eV |
|  |  | Ar | $10^6$ | X | Mn, 1.48eV |

for thermal conversion, as reported by Klein et al (Ref 15) and Hallais (Ref 11). The 1.41 eV peaks in the $N_2$-annealed samples are fully as large as those in the converted $H_2$-annealed samples, but the $N_2$-annealed samples did not convert; further, they retained the highest resistivity of any of the annealed samples. Mn is completely absent from several other samples which did convert, as can be seen in table 2.

Other than Mn, the only change in the $H_2$ annealed, Cr-doped samples was the growth of the Si peak, which also occurred in all $Si_3N_4$ capped, non-epitaxial samples and in the $N_2$-annealed samples, none of which converted. However, the Si peaks in these samples are small compared to the Si peaks in the converted $H_2$-annealed samples; thus Si may be responsible for the conversion of these samples. No other changes in their spectra were found.

Among the undoped samples, the C-peak grew sharply in the converted samples but did not appear at all in the unconverted sample. The Cu acceptor -As vacancy peak also grew in the Ar-annealed, capped sample which converted, but was not observed in the other undoped, converted samples. Although it did not grow after annealing in any unconverted samples, it was present with comparable size in several samples which did not convert. It therefore seems unlikely that Cu is in itself a cause of thermal conversion.

Although Ar-annealing prevented conversion in all samples except WBN6/24 and epitaxial samples, the resistivities of Ar-annealed samples were typically as low as the resistivities of converted samples. $N_2$-annealing produced better results, as can be seen in tables 1 and 2.

## V Conclusions and Recommendations

In this thesis, the photolumunescence spectra of a number of GaAs samples were studied in order to learn more about the causes of thermal conversion. From an examination of these spectra and comparison with their electrical properties, it is concluded that, for these samples, conversion is associated with at least three different mechanisms. In the epitaxial samples conversion appears to be caused by either the tin which contaminated the epitaxial growth system (see sample data), or an unknown impurity associated with tin, or both. In the undoped samples, conversion is associated with an increase in the surface concentration of carbon impurities. In the chromium-doped samples, conversion appears to be connected with the appearance of silicon. Manganese was effectively ruled out as a cause of conversion, as it was shown to come and go in some samples without affecting their electrical properties.

It should be noted that, while these conclusions are believed to be valid for this group of samples, this study indicated that conversion can be caused by any of a number of impurities.

In general, $H_2$-annealed samples converted to p-type when uncapped. Capped $H_2$-annealed samples and both capped and uncapped Ar-annealed samples did not convert but showed decreased resistivity, and $N_2$-annealed samples maintained a semi-insulating surface. No conclusions were reached as to the mechanism by which the different atmospheres affected the conversion process.

Although annealing in argon was for the most part effective in preventing the conversion of the surface layers to p-type, samples annealed in argon and hydrogen-annealed samples which did not convert showed very low resistivity surface layers with mixed conductivities. As this condition can be as detrimental to the performance of semiconductor devices as conversion to p-type, the suggestion by Hallais (Ref 11:227) that samples be annealed in argon in the future seems to be of little value. A better choice might be nitrogen, which not only prevented conversion but allowed the samples to retain high resistivities. Further research into the effects of annealing capped and uncapped GaAs in nitrogen is therefore recommended.

It is further recommended that this study be continued with chromium doped, epitaxial layer samples at such time as the tin is removed from the AFWAL epitaxial growth facilities. Also, secondary ion mass spectroscopy (SIMS) measurements on converted and unconverted samples would be of great value in verifying the conclusions reached in this thesis.

# Bibliography

1. Lum, W.Y., *et al*. "Thermal Degradation of Homoepitaxial GaAs Interfaces", *Applied Physics Letters*, 30 : 1-3 (January 1977).

2. McKelvey, J.P. *Solid State and Semiconductor Physics*. New York: Harper and Row, 1966.

3. Pankove, J.I. *Optical Processes in Semiconductors*. Englewood Cliffs New Jersey: Prentice-Hall, Inc., 1971.

4. Willardson, R.K. and A.C. Beer. *Semiconductors and Semimetals, Vol 8 - Transport and Optical Phenomena*. New York: Academic Press, 1972.

5. Colbow, K. "Free-to-Bound and Bound-to-Bound Transitions in CdS," *Physical Review, 141*: 742-749 (January 1966).

6. Edmond, J.T. "Heat Treatment of Gallium Arsenide", *Journal of Applied Physics, 31*: 1428-1430 (August 1960).

7. Wysocki, J.J. "Thermal Conversion in n-type GaAs", *Journal of Applied Physics, 31*: 1686-1689 (September 1960).

8. Hwang, C.J. "Photoluminescence Study of Thermal Conversion in GaAs Grown from Silica Boats", *Journal of Applied Physics, 39*: 5347-5356 (November 1968).

9. Chang, L.L., *et al*. "Vacancy Association of Defects in Annealed GaAs", *Applied Physics Letters, 19*: 143-145 (September 1971).

10. Lum, W.Y., and H.H. Wieder "Thermally Converted Surface Layers in Semi-Insulating GaAs", *Applied Physics Letters, 31*: 213-215 (August 1977).

11. Hallais, J., *et al*. "Properties and Thermal Conversion of Semi-Insulating GaAs", *Institute of Physics Conference Number 33b*. 220-227, April 1974.

12. Zucca, R. "Effects of Heat Treatment on Semi Insulating GaAs", *Institute of Physics Conference Number 33b*. 228-235, April 1974.

13. Ohno, H., et al. "Thermal Conversion Mechanism in Semi-Insulating GaAs", Journal of Applied Physics, 50: 8226-8228 (December 1979).

14. Klein P.B., et al. "Thermal Conversion in GaAs", Unpublished paper, Naval Research Laboratory, Washington, D.C. 1980.

15. Ashen, D.M., et al. "The Incorporation and Characterization of Acceptors in Epitaxial GaAs", Journal of Physics and Chemistry Solids, 36: 1041-1053 (March 1975).

# Appendix

## Photoluminescence of Cr-doped GaAs Before and After Annealing

Spectra of Cr-doped GaAs samples shown in the body of this thesis are from sample CS4679/75. The spectra of other Cr-doped samples which were used in this study are shown here for completeness.

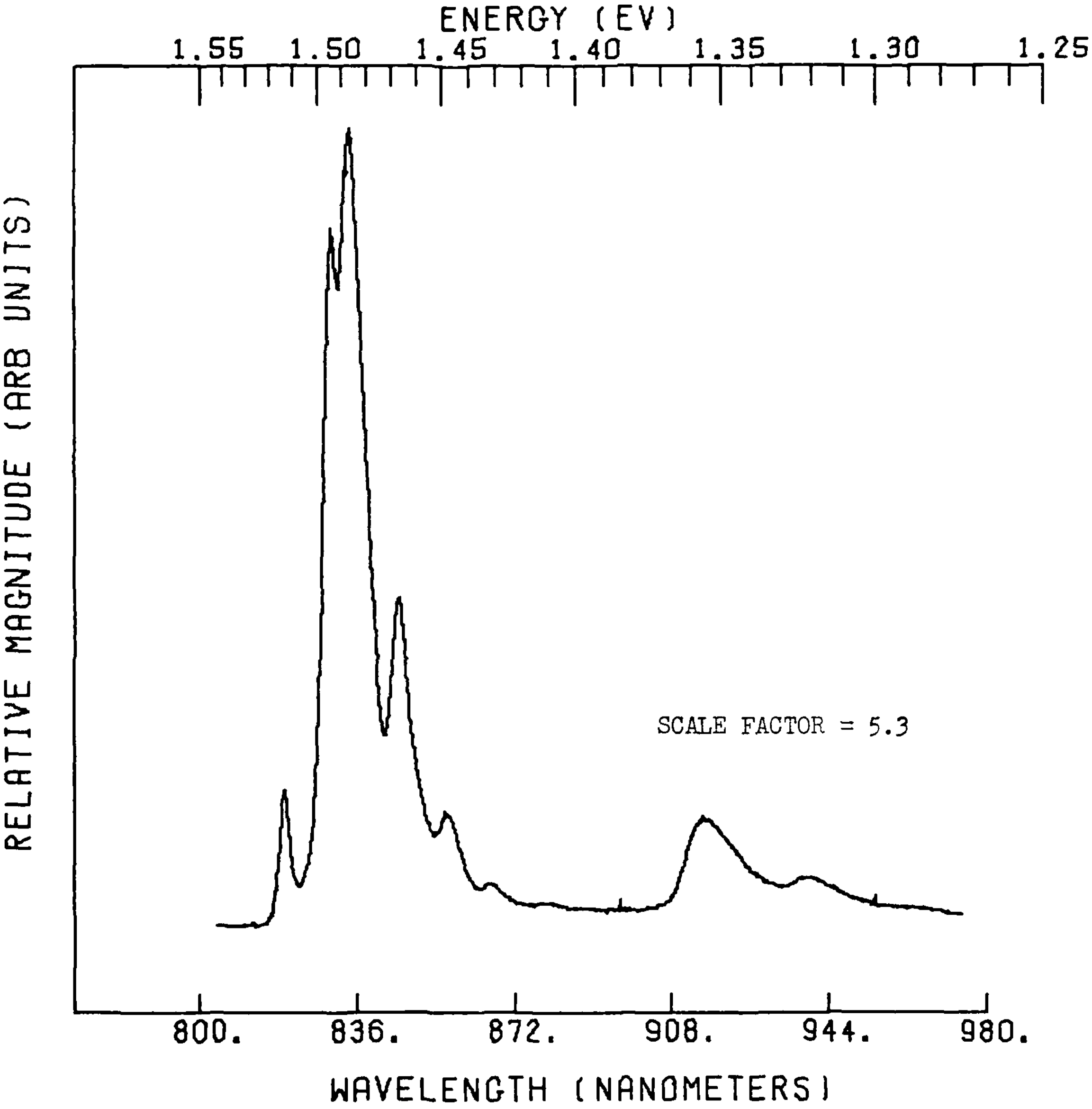

Figure A-1. Photoluminescence of Sample CS4679/66 Before Annealing.

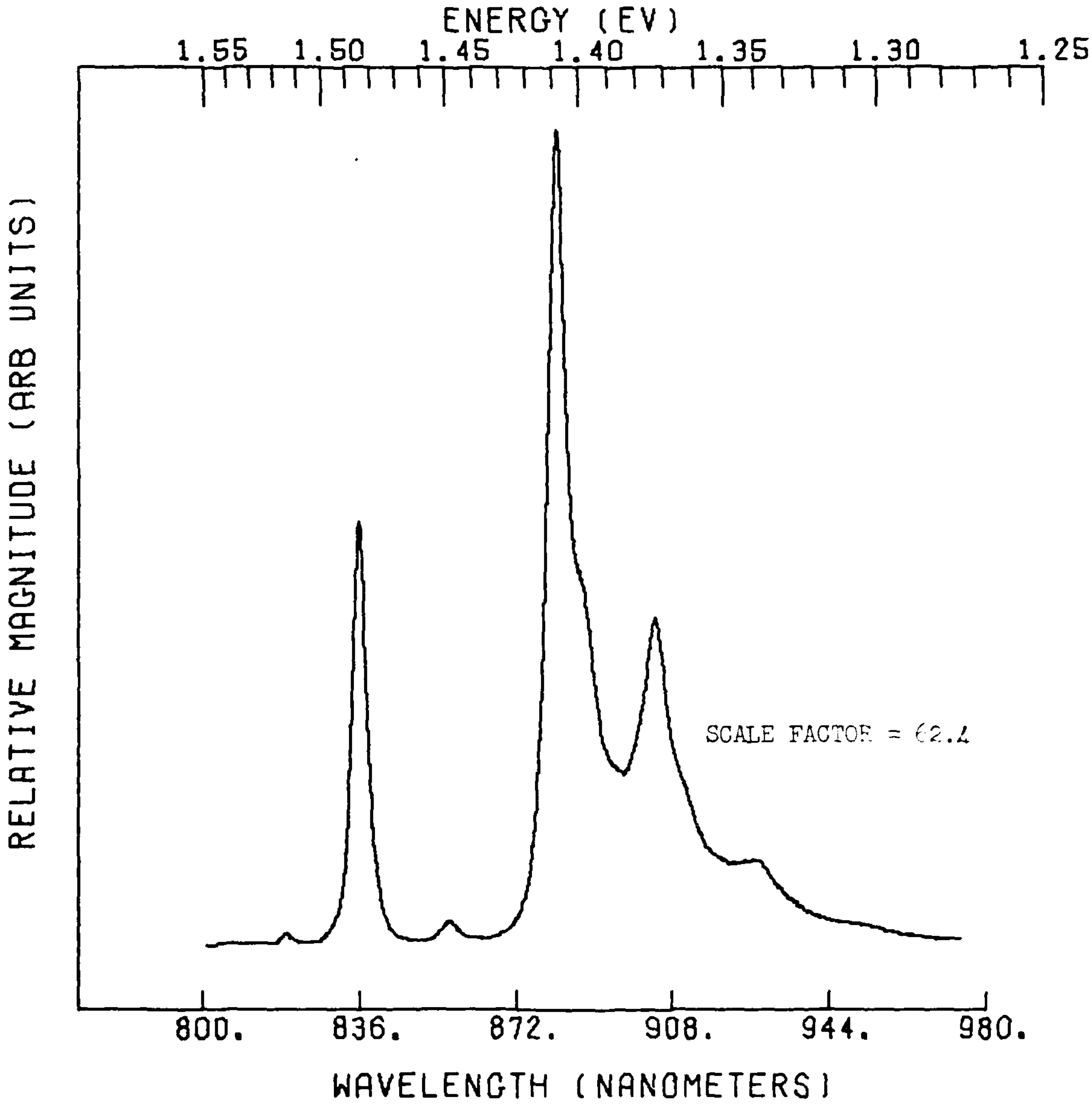

Figure A-2. Photoluminescence of Sample CS4679/66 After Annealing in $H_2$ at 850°C for 20 Minutes.

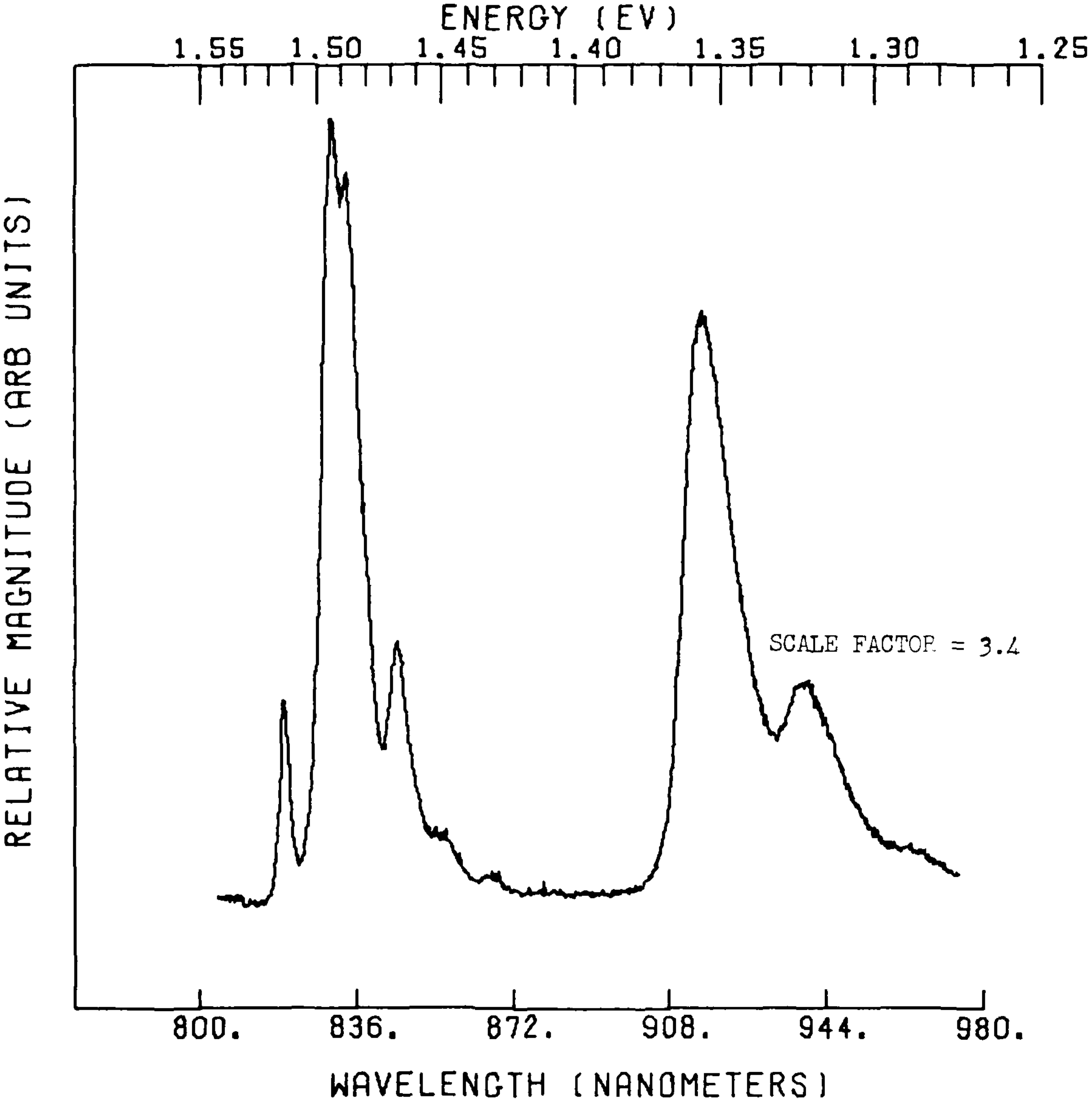

Figure A-3. Photoluminescence of Sample CS4679/73 Before Annealing

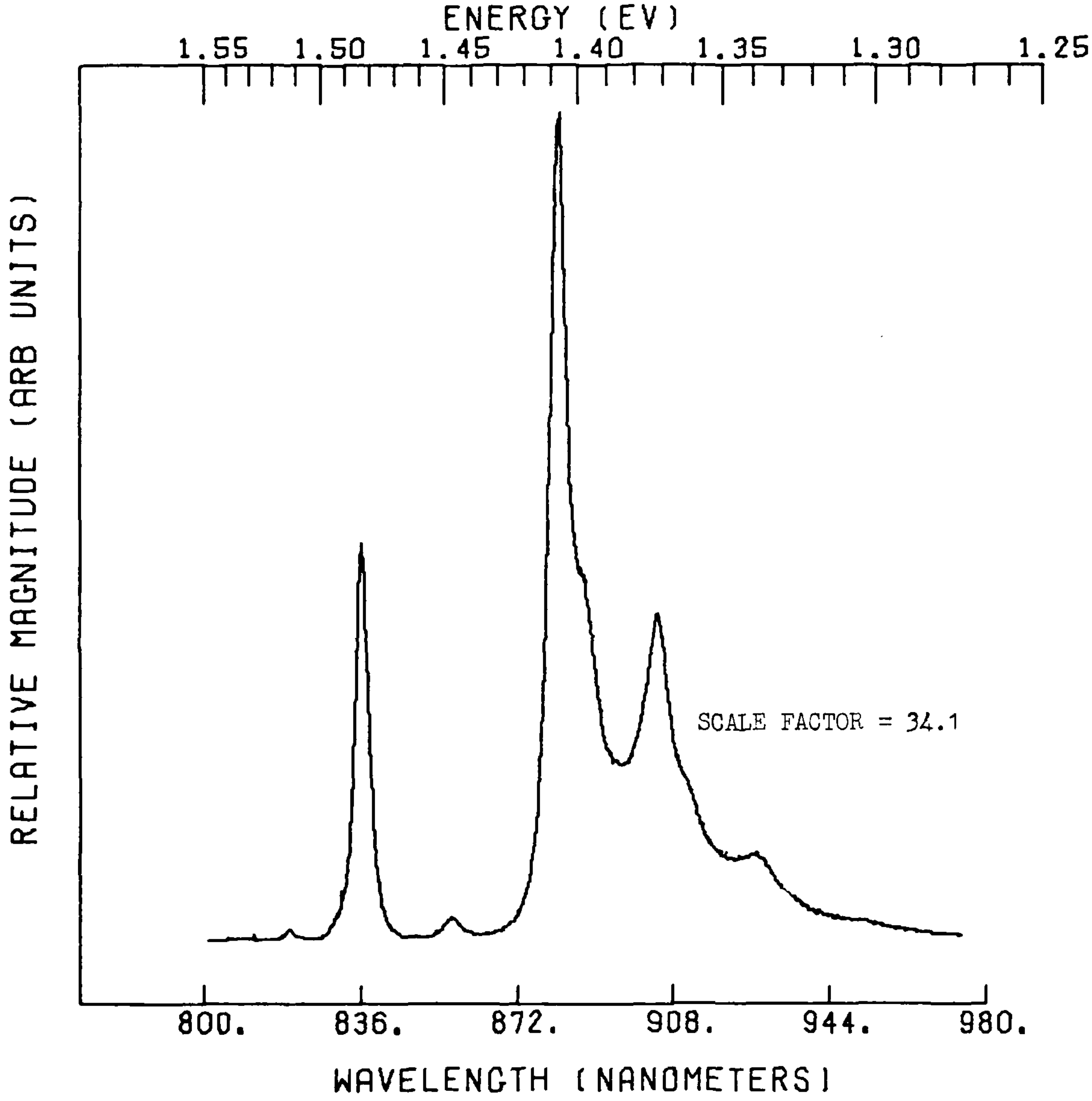

Figure A-4. Photoluminescence of Sample CS4679/73 After Annealing in $H_2$ at 850°C for 20 Minutes.

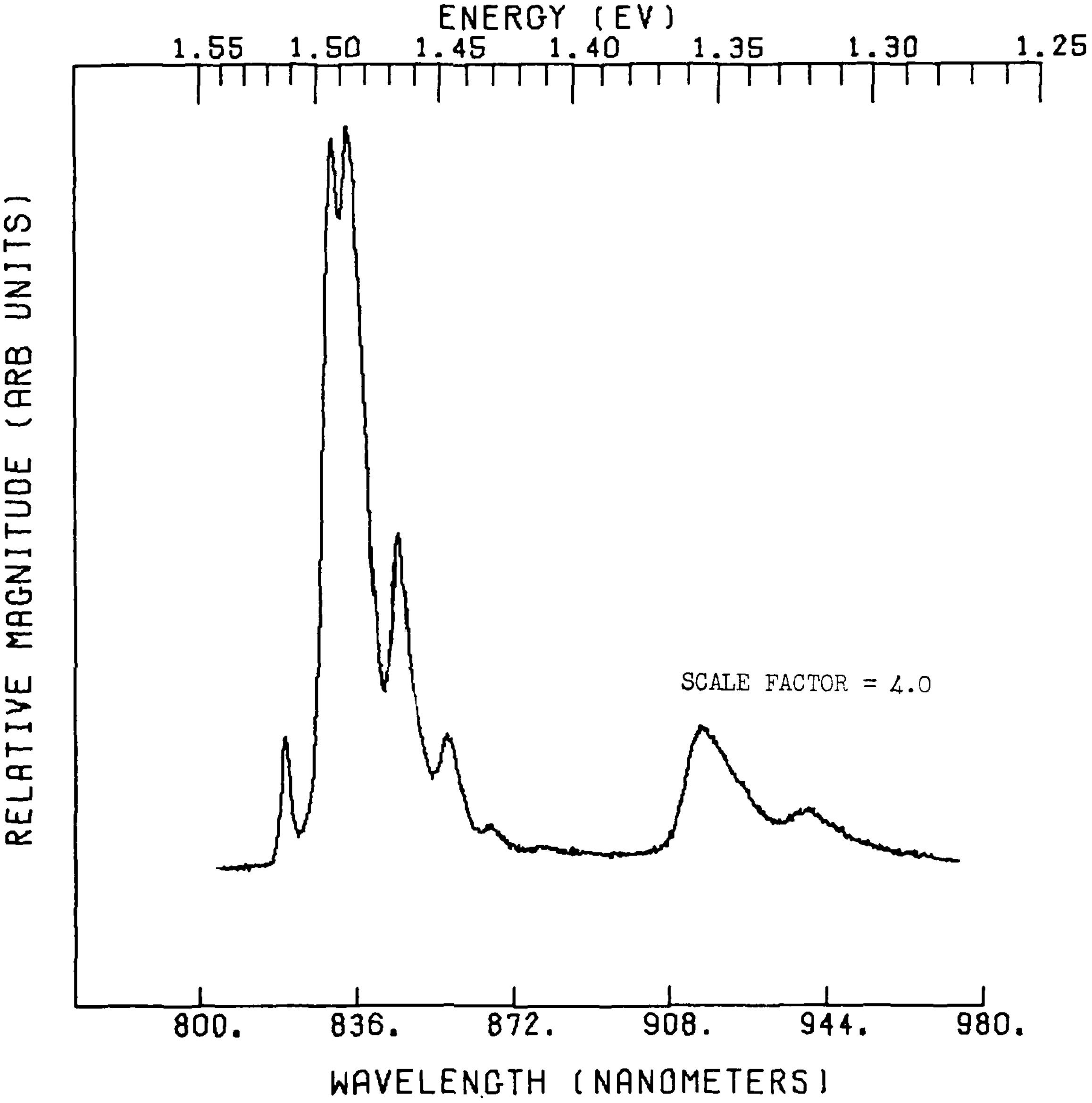

Figure A-5. Photoluminescence of Sample CS4679/78 Before Annealing

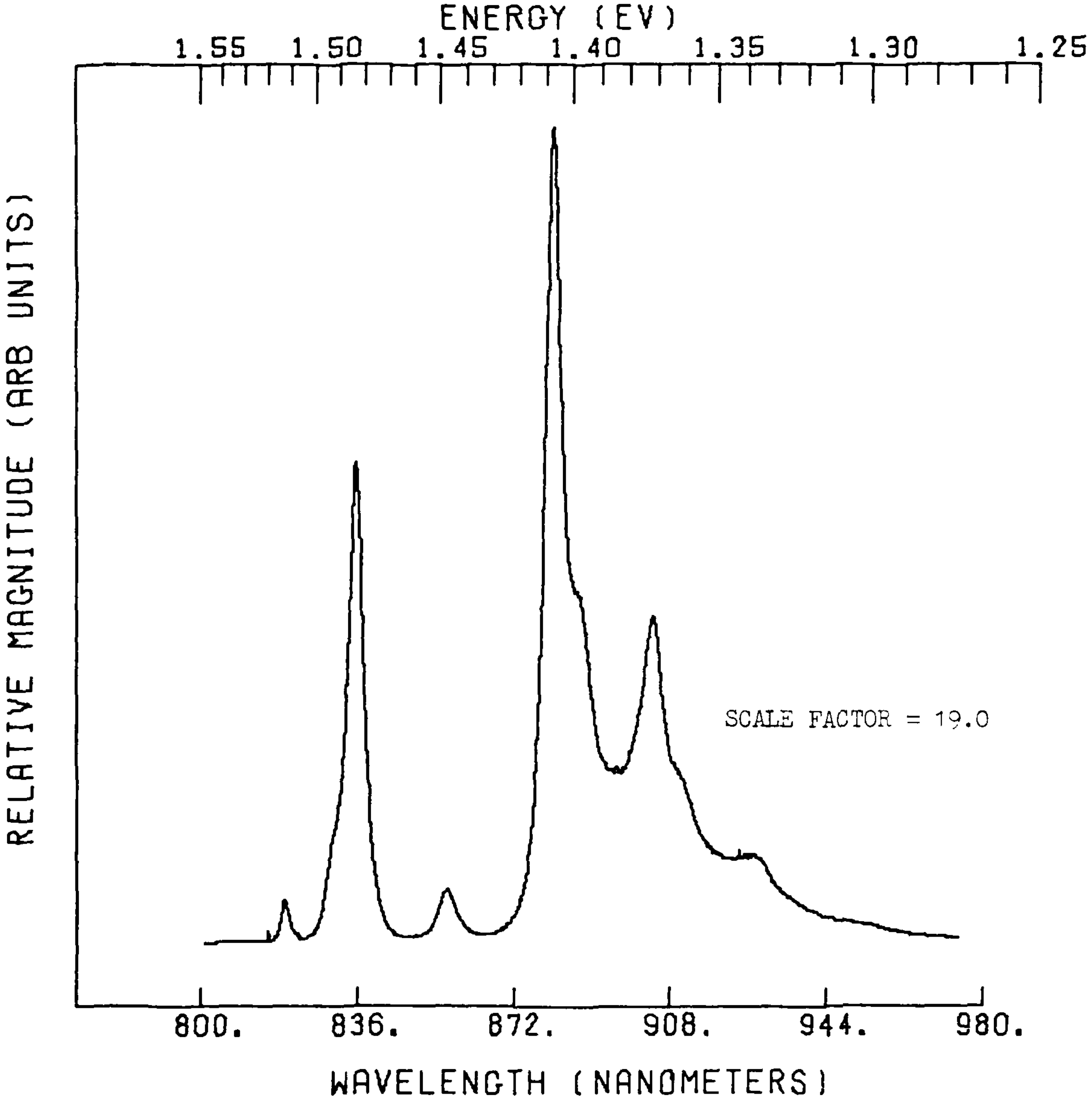

Figure A-6. Photoluminescence of Sample CS4679/78 After Annealing in $H_2$ at 850°C for 20 Minutes.

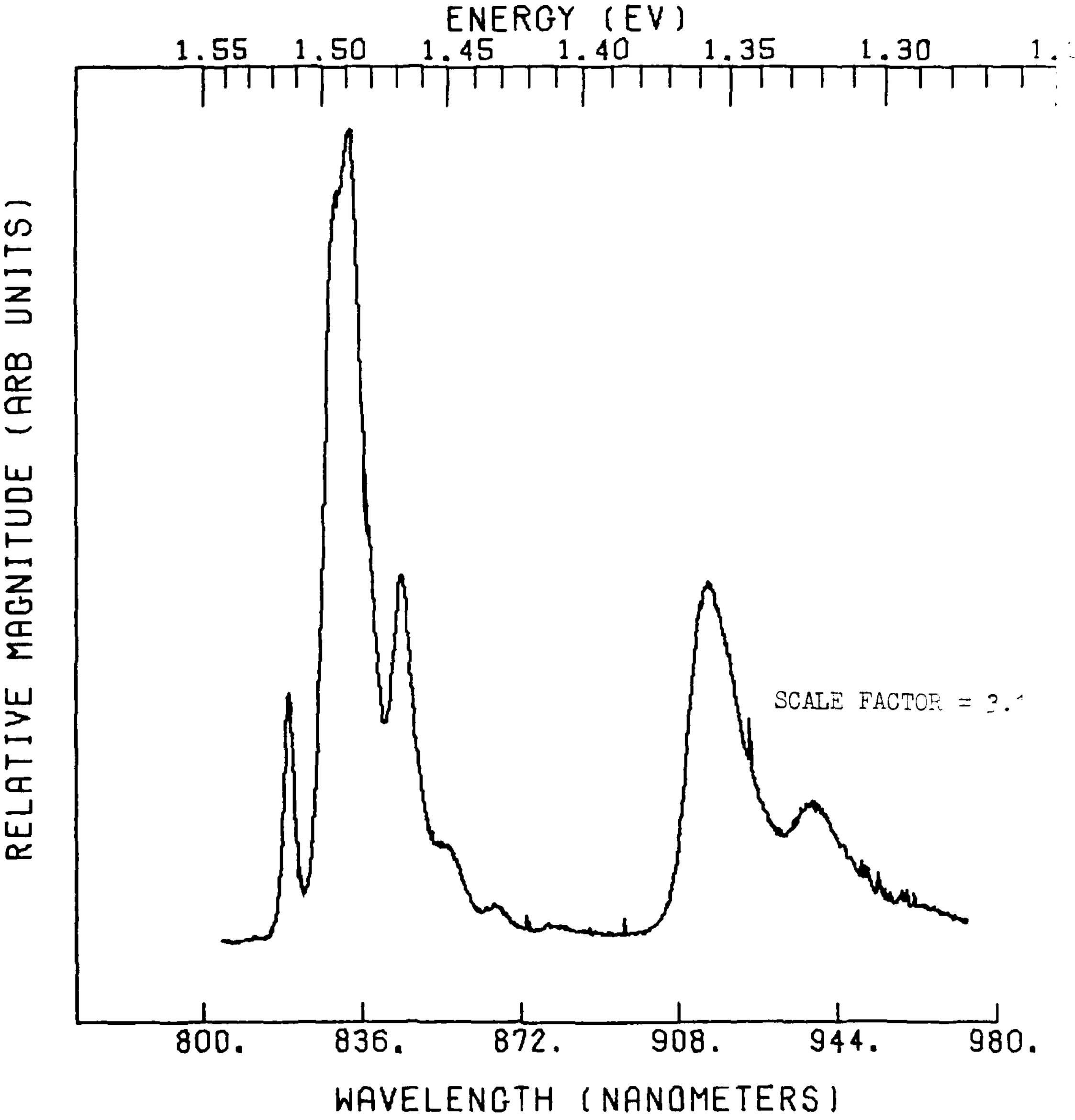

Figure A-7. Photoluminescence of Sample CS4679/77 Before Annealing.

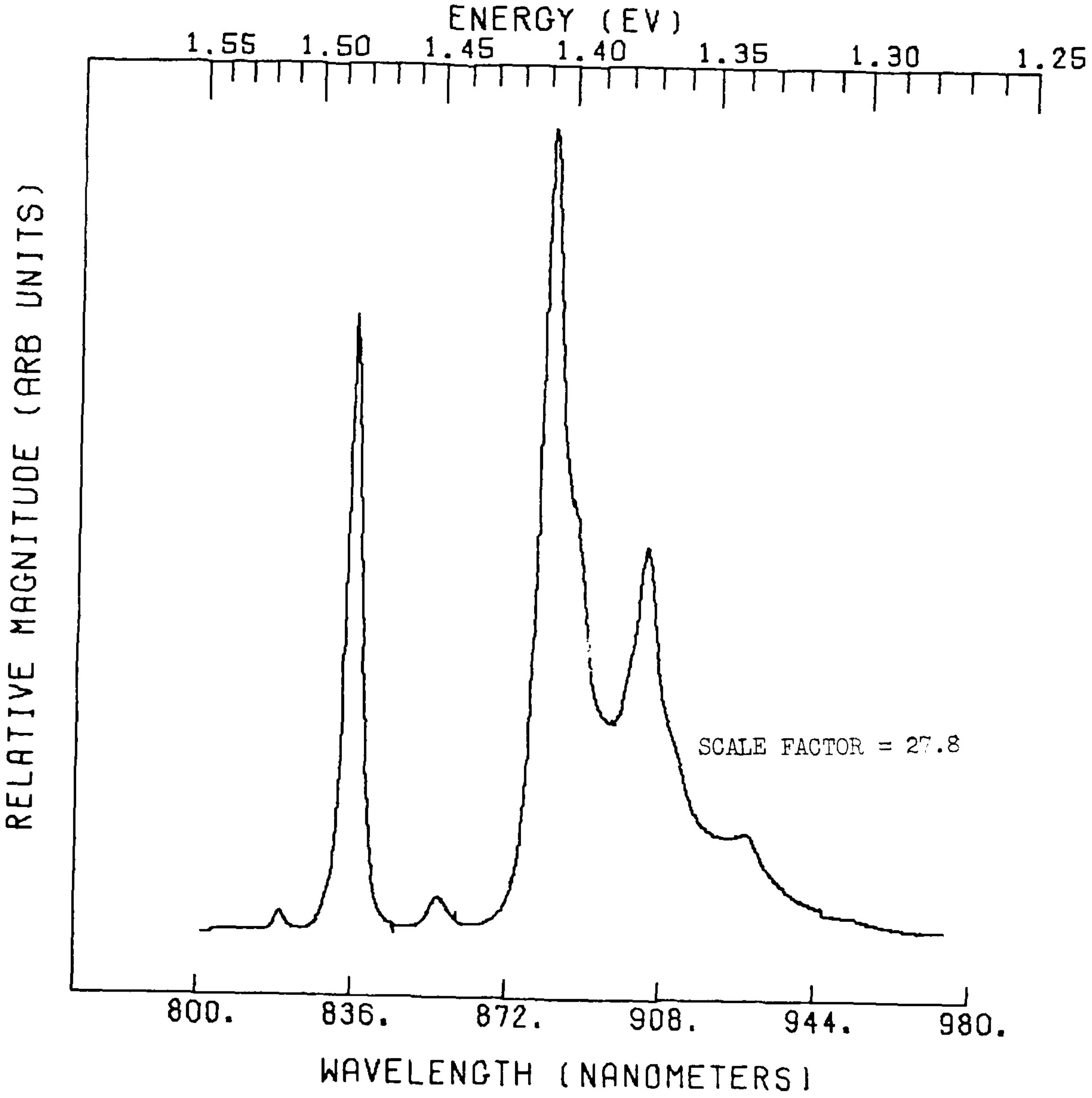

Figure A-8. Photoluminescence of Sample CS4679/77 After Annealing in $H_2$ at 850°C for 20 Minutes.

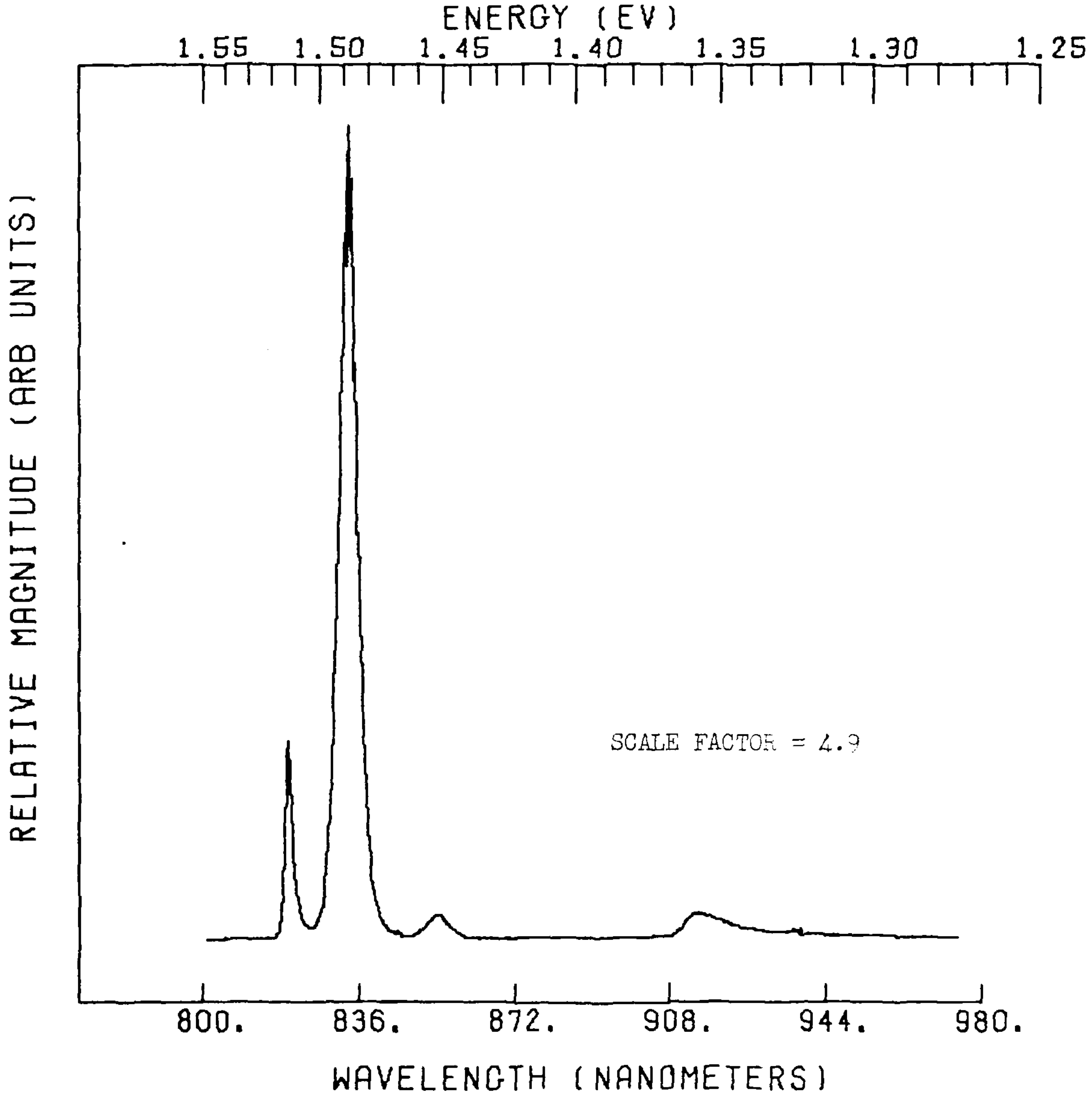

Figure A-9 Photoluminescence of Sample CS4679/77 After Annealing in Ar at 850°C for 20 Minutes.

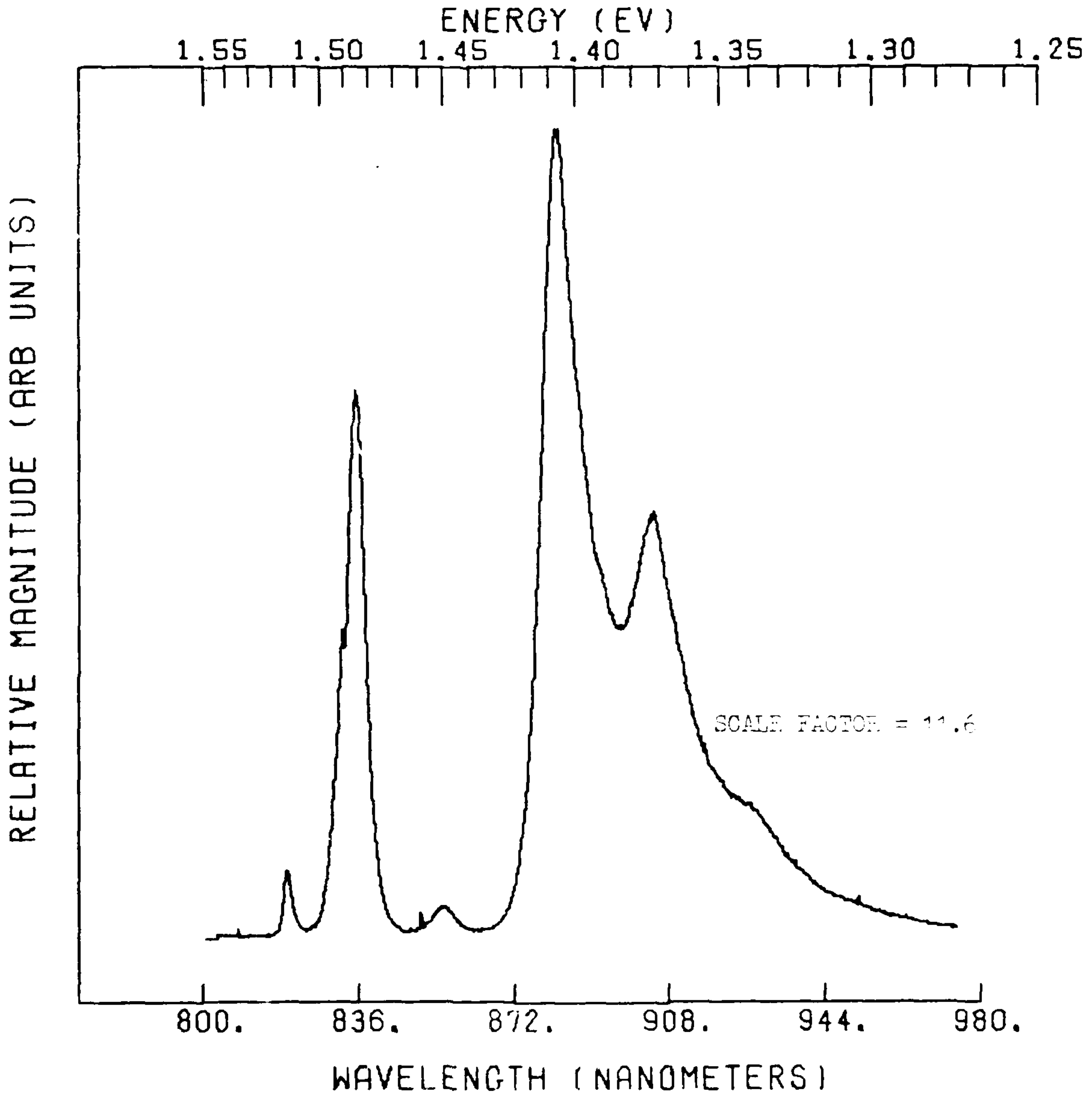

Figure A-10. Photoluminescence of Sample CS4679/77 After Annealing in $N_2$ at 850°C for 20 Minutes.

# Vita

John McLemore Anderson was born on 26 August 1955 in San Antonio, Texas. He graduated from high school in Macon, Mississippi in 1973 and attended Mississippi State University from which he received the degree of Bachelor of Science in Electrical Engineering in May 1977. Upon graduation, he received a commission in the USAF through the ROTC program. He was assigned to Kelly Air Force Base, Texas, where he served as an electrical engineer with the San Antonio Air Logistics Center until entering the Air Force Institute of Technology in June 1979.

Permanent Address: 307 Bradshaw Street
Macon, Mississippi 39341

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

| | | |
|---|---|---|
| **REPORT DOCUMENTATION PAGE** | | READ INSTRUCTIONS<br>BEFORE COMPLETING FORM |
| 1. REPORT NUMBER<br>AFIT/GEO/PH/80-1 | 2. GOVT ACCESSION NO.<br>AD-A094400 | 3. RECIPIENT'S CATALOG NUMBER |
| 4. TITLE (and Subtitle)<br>Photoluminescence Study of Thermal Conversion in Gallium Arsenide | | 5. TYPE OF REPORT & PERIOD COVERED<br>MS Thesis |
| | | 6. PERFORMING ORG. REPORT NUMBER |
| 7. AUTHOR(s)<br>10 John M. Anderson<br>1st Lt. USAF | | 8. CONTRACT OR GRANT NUMBER(s)<br>(9) Master's thesis |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>Air Force Institute of Technology (AFIT/EN)<br>Wright Patterson AFB , Ohio 45433 | | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS<br>(11) |
| 11. CONTROLLING OFFICE NAME AND ADDRESS<br>Air Force Wright Aeronautical Laboratories (AFWAL)<br>Wright Patterson AFB, Ohio 45433 | | 12. REPORT DATE<br>Dece[redacted]80 |
| | | 13. NUMBER OF PAGES<br>72 |
| 14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)<br>(12) 86 | | 15. SECURITY CLASS. (of this report)<br>Unclassified |
| | | 15a. DECLASSIFICATION DOWNGRADING SCHEDULE |

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Approved for Public Release; IAW AFR 190-17

06 JAN 1981

FREDERICK C. LYNCH, Major, USAF
Director of Public Affairs

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Gallium Arsenide
III-IV Compounds
Thermal Conversion
Photoluminescence

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A photoluminescence study was made of undoped and chromium-doped gallium arsenide annealed in three different atmospheres: argon, hydrogen, and nitrogen. The purpose of this study was to determine the causes of thermal conversion and to examine the effects of different annealing atmospheres on this problem. It was found that conversion can be due to any of a number of causes, rather [illegible] causes. Conversion in the samples studied was [illegible] samples

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

012225

(Block 20 continued)

and with silicon in doped samples. Although manganese was found to be present in many samples, no clear association of manganese with type conversion was found. It was found that annealing under nitrogen gas was the most effective way of maintaining a semi-insulating surface layer.

DAT

FILM