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RESEARCH ESTABLISHMENT

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ABSTRACT

Contacts formed by laser doping single crystal semiconducting samples have been investigated by a variety of techniques. p- and n-type contacts have been formed on Ge, Si and GaAs by irradiating evaporated surface layers with a Q-switched ruby laser. The contacts produced were thin and heavily doped. Techniques used to examine the contacts include Rutherford backscattering, scanning electron microscopy and sheet Hall and resistivity measurements.

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ELECTRIC CONTACTS; ANNEALING; DOPED MATERIALS; GERMANIUM; SILICON; GALLIUM ARSENIDES; LASER RADIATION; P-N JUNCTIONS; P-TYPE CONDUCTORS; N-TYPE CONDUCTORS

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(Continued)

CONTENTS (cont.)

1. INTRODUCTION

At present, it appears that the laser annealing process may prove to be a suitable alternative, or even superior method to that of furnace annealing ion implanted contacts. Much effort, mostly with Si but also with GaAs and Ge, is being directed to the study of this process. Considerably less effort, however, has gone into assessing the closely related technique of producing contacts directly by laser doping. The present work was undertaken to evaluate the contacts produced by the latter technique.

Laser annealing an ion implanted semiconductor (Si) was first reported by Khaibullin et al.[1974] and subsequently investigated in many laboratories throughout the world [White et al. 1979]. While actively involved in laser-annealing studies at Oak Ridge National Laboratory (ORNL), Narayan et al. [1978] reported the production of a p-n junction when laser doping Si. They irradiated a vacuum-deposited B layer with the output pulse from a Q-switched ruby laser. Much earlier, Fairfield and Schwuttke [1968] had shown that junctions could be formed but only for spot sizes <1 mm^2. The most commonly used lasers are the pulsed Q-switched ruby or Nd:YAG and the continuous wave (CW) Ar ion. All contacts described in this report were produced with a Q-switched ruby laser; the semiconductors were Ge and Si and, to a lesser extent, GaAs.

It should be noted that the laser is simply a source of energy which is used to melt and thereby either anneal or dope a surface layer. Alternative energy sources are pulsed electron and ion beams and these are being examined in other laboratories.

This report outlines briefly the laser-doping process and describes the experimental contact fabrication procedures at the AAEC laboratories. The contacts are being investigated by a variety of techniques and some preliminary data are presented - mainly on thickness, impurity concentration and electrical activity. Certain conclusions are drawn from the data which correlate these parameters.

In general, many techniques are available to characterise laser-doped contacts. This report seeks to describe only those techniques which have been used in this laboratory and to present results representative of those which have been obtained and are reproducible. There is no intention to imply that these techniques are necessarily superior to others. Some comments on other useful techniques have been added.

2. CONTACT FORMATION

2.1 Mechanism

In the laser-doping process, a thin surface layer acts as a source of dopant when irradiated with a high-intensity pulsed laser. There is considerable evidence that the laser melts a surface layer of the semiconductor. Most convincing perhaps are the time-resolved reflectivity measurements [Auston et al. 1978] of the surface of an ion-implanted Si wafer; these show an abrupt increase in reflectivity during the initial portion of the annealing pulse. In many cases, surface morphology suggests the presence of a liquid layer. It should be pointed out, however, that there is some theoretical [Van Vechten et al. 1979] and some experimental [Lo and Compan 1980] work which does not support the melting hypothesis. On solidification, regrowth is epitaxial and the impurity is incorporated in the crystal, ideally in an electrically active substitutional site.

Typical pulse lengths for Q-switched lasers are 10-100 ns and the energies required for melting are in the range 1 - 2 J cm^{-2}. It should be noted that strictly speaking these energies are those which allow laser annealing. The energy required for laser doping may be greater than this owing to the different reflectivity of the surface dopant layer. Commonly, this dopant is a metal with a high reflectivity. The actual temperature attained by the surface will depend on laser energy and pulse length as well as on the optical properties of the dopant layer and semiconductor substrate. The time during which the surface is molten is obviously a function of the same parameters and is always greater than the laser pulse length. Models have been proposed [Wang et al. 1978, Baeri et al. 1979] describing the melting of a surface layer followed by liquid phase epitaxy.

2.2 Experimental Details

A Q-switched ruby laser (λ = 0.6943 μm) has been used for all the measurements described in this report. The full width at half maximum (FWHM) of the output pulse was 25 ns. Since this pulse was not spatially uniform, it was passed through a homogeniser before striking the sample. This homogeniser was of the type described by Cullis et al. [1979] and made from Perspex rod (ϕ = 20 mm). The transmission of such a device is typically ~50%. It was observed that the Perspex homogenisers were subject to radiation damage and had a useful life of between 10 and 20 pulses, depending on the output energy; when damage became obvious the homogeniser was replaced. The homogenisers were produced with three different exit diameters (8,10 and 16 mm). The output energy ranged to a maximum of ~6 J at 2400 V, the maximum applied potential on the flash lamp capacitor bank; the laser was usually operated in the lower half of this energy range. The actual output energy density of the homogeniser is a function of its transmission, output diameter, stored energy in the capacitor bank and laser operating conditions. Laser conditions were held constant and the capacitor bank applied potential varied.

The samples were prepared by lapping them on glass with a slurry of 600# SiC grit in water. They were then etched for five to seven minutes in a warm solution of four parts (by volume) HNO_3 to one part HF. This produced a very clean, highly polished surface. If necessary, the opposite face of the sample was masked with Apiezon wax which was further protected with masking tape (MMM Electroplating Tape No-470). After washing in de-ionised water, and drying with filtered N_2 gas, the sample was placed in a vacuum evaporation system where a thin layer of a suitable dopant was laid on the surface. Evaporation was performed using an ohmically heated Mo filament in a vacuum better than 5×10^{-6} mm Hg.

Film thicknesses were not measured directly but obtained qualitatively from the resistance between two copper electrodes on a sheet of glass. At all times, the films were semi-transparent with thicknesses estimated to be ≤ 30 nm. Table 1 lists elements which have been evaporated and subsequently irradiated by the laser. After irradiation, excess metal was removed by soaking in warm HCl for 10 to 15 minutes. It should be noted that these elements, as would be expected, are common dopants of Si and Ge. Boron and arsenic were not investigated for practical reasons but, provided that a suitable method can be found for laying down a thin layer, the technique would still be suitable. In future, boron will be evaporated in a sputtering system.

Another apparent omission from Table 1 is P. However, a method was suggeste [Donovan 1960] whereby a thin layer of a P-loaded solution is painted on the surface before laser irradiation. The recipe requires 20 parts (by volume) of 2-butoxy ethanol to 1 part P_2O_5. This process was successful, producing evidence for the doping of Ge and Si. No doping was found when the solvent was used without P_2O_5 .

2.3 Initial Checks

After soaking in HCl to remove excess metal, two initial checks were commonly made: first,to determine that melting had taken place and second, to show that electrical doping had occurred.

The sample was first examined under an optical microscope. Evidence for melting was found in the surface morphology. Figure 1 shows a slightly exaggerated version of the typical 'orange peel' texture which was observed. The existence of this texture was used as a criterion for melting. However, it is possible that such a surface texture may be indicative of excess energy.

In some samples, presumably with energies closer to the threshold for melting, the texture was very fine and hard to see. In others (such as Figure 1), the melting pattern was very obvious.

It was very difficult to melt highly polished Ge and Si samples which did not have a surface layer. In this situation, much energy was being lost by reflection and the critical amount for melting was not absorbed.

For some Ge samples, an additional thin ($\lesssim$ 30 nm) layer of Ge has been evaporated over the dopant layer. The optical coupling between sample and laser can be improved by this amorphous layer, since it is more absorbing than the polished single crystal substrate and the metallic surface dopant. In addition, there is evidence that an amorphous layer melts at a lower temperature than crystalline material [Bagley and Chen 1979].

Occasionally non-uniformities were observed in the orange peel texture suggesting that the energy density was not uniform throughout the output beam area. This can arise if sample and homogeniser exit face are not kept close together and plane parallel. In addition, if the input face is not sufficiently diffusing, patterns (i.e. inhomogeneities) are found inside the beam area.

The samples were examined for indications of doping using a two-point probe based on the Seebeck effect. This thermal probe has two Pt points, one of which is at room temperature while the other is held at ~100°C. This type of probe is commonly used to give the conduction polarity and a qualitative indication of the degree of doping in Ge and, with reduced sensitivity, in Si. It has also proved useful for GaAs laser-doped with Sn (n-type) and Zn (p-type).

It should be noted that it may be possible to damage the thin surface layer if these probes are used. Consideration must therefore be given to the subsequent tests and other uses of the sample before probing is carried out. If, for example, a diode is to be made, it is inadvisable to thermally probe the thin contact; mechanical damage can lead to injection and poor reverse leakage current.

3. ELECTRICAL EXAMINATIONS

3.1 p-n Junctions

An obvious test of a laser-doped contact is to fabricate a p-n junction and examine the associated I-V characteristic. Since one of the aims of this work was to investigate the possible use of laser-doped contacts in nuclear radiation detectors [Lawson 1981], this type of examination was commonly made. In particular, the leakage current under reverse bias conditions was investigated since it is critically related to detector performance. Diodes were made on Ge and Si of the appropriate conduction type,using the elements listed in

Table 1 and phosphorus 'paint'. In general, it was found that under reverse bias, the leakage currents are higher than those obtained by conventional contacting techniques, and that in the forward direction the characteristic is less steep. Such behaviour may be due to inhomogeneities in the output (after the homogeniser) beam or to damage in the junction region as a result of excessive laser energy. The damage may take the form of carrier trapping and generation centres. Nevertheless some p-n junctions have shown good leakage currents. Therefore, once the question of the appropriate laser energy has been resolved, it will be possible to produce routinely p-n junctions with good I-V characteristic.

It seems likely that only a fairly narrow range of energy densities will be useful. Below this range, melting will not take place, and above it, damage will occur.

3.2 Sheet Resistivity and Hall Measurements

Measurements have been made of the sheet resistivity (ρ_S) and the sheet Hall coefficient (R_S) associated with laser-doped layers. The procedure has been described by Van der Pauw [1958]. The sheet Hall coefficient allows the calculation of N_S - the carrier concentration per unit area. The effective Hall mobility (μ_{eff}) was determined from the relation

$$\mu_{eff} = (\rho_S N_S e)^{-1}$$

where e is the electronic charge (1.6×10^{-19} C). In most cases, the doped layer was formed on a substrate of the opposite polarity, thus removing the shunting effects of base material.

A sample holder made of non-magnetic materials allowed contact at four approximately equally spaced points on the sample periphery. Electrical contact was made by spring Be-bronze probes, with small Au pads covering the tips to prevent them scratching the thin surface layer. The magnet was a C-shape permanent magnet with a 4.4 cm gap and 4.2 cm pole diameter. The magnetic field was measured with a rotating coil gaussmeter to be 2.7 kG.

Table 2 presents values of sheet resistivity, carrier, concentration and effective Hall mobility for a number of laser-doped Ge samples.

3.3 Ohmic Contacts

Laser-doped contacts can, of course, be ohmic too; a number of studies have been reported in the literature particularly on contacts applied to GaAs [Eckardt 1980]. Using an evaporated Sn layer, ohmic contacts to n-type GaAs have been made in the AAEC laboratories. The ohmicity of these contacts was assessed by examining the linearity of the I-V characteristic. The linearity was characterised by the correlation coefficient of a least squares analysis and by a voltage cut-off point beyond which the I-V became non-ohmic.

The results of these investigations obtained by measuring the I-V between two laser-doped contacts on a substrate of the same conduction polarity are shown in Table 3.

4. NUCLEAR EXAMINATIONS

4.1 Rutherford Backscattering (RBS)

Backscattering and channelling measurements were performed on the AAEC's Van de Graaff accelerator at Lucas Heights. The 2.0 MeV incident He^+ ions were detected, after backscattering, in an Si nuclear radiation detector set at 170°. The detector energy resolution was typically 18 keV FWHM; this is equivalent to a depth resolution of 30 nm for Ge and GaAs, and 40 nm for Si. The sample was mounted on a goniometer which could be adjusted from outside the vacuum system. This allowed both random and channelled data to be collected. Spectra, such as those shown in Figure 2, demonstrated that the impurity had been incorporated into the semiconductor. The vertical arrow denotes the energy (channel) of the He^+ ions after scattering from a Ga nucleus on the surface. The profile of the Ga peak has an FWHM of 70 nm, indicating that mixing has occurred to a depth of ~60 nm.

Further results from backscattering analyses are shown in Table 4. The parameter $\chi_{min.}$ is the ratio of the yield from the substrate behind the surface peak in the channelled and random directions. It is a measure of the crystalline quality of the material and is typically three to five per cent in good quality material. The data in Table 4 show that, as might be expected, the quality deteriorates (i.e. $\chi_{min.}$ increases) with increasing impurity concentration. It can be seen that very large amounts of impurity can be incorporated, especially in the case of Sb in Ge. The difference between random and channelled impurity concentrations gives the substitutional concentration which here is ≤1 per cent.

It should be noted that a substitutional fraction of ~1 per cent gives solubilities which are considerably higher than the equilibrium values. This effect has already been observed in Si [Fogarassy et al.1980; White et al. 1980] but not as yet reported for Ge. If the metal layer is covered with a thin evaporated layer of the substrate material, it appears to allow a higher substit-tutional fraction, at least for the case of In on Ge, where up to 1.6 atom per cent has been measured. However, this effect may also be related to the dopant layer thickness which is not accurately known.

By combining the maximum substitutional concentration with the FWHM of its distribution, a crude estimate can be obtained for the electrically active concentration per unit area. This may then be compared with the value obtained by Hall measurements. The values obtained by both methods are in fair agreement, as can be seen in Table 5.

4.2 Radiation Detector: α-Particle Resolution

Although RBS gives a direct measurement of the contact thickness, it is only useful if the mass of the impurity atom is greater than that of the host lattice atom. Another method for assessing contact thickness, which is independent of the impurity mass, requires the construction of a semiconductor nuclear radiation detector having a front laser-doped contact.

The resolution of semiconductor detectors for heavily ionising radiation (normally α-particles) is a function of the contact thickness, provided of course that the contributions to the resolution from the electronic system and from the source are small. Examinations at Lucas Heights have provided qualitative information only, although it is possible to obtain quantitative information under certain conditions [Elad et al. 1973].

Figure 3 shows the spectrum of α-particles from a ^{241}Am source recorded by a Ge detector with a laser-doped In contact. The good resolution of the 5443 MeV line demonstrates that the contact is thin.

4.3 Scanning Electron Microscope

The scanning electron microscope (SEM) was used to investigate the laser-doped contacts. Although not strictly a nuclear technique, it seems more appropriate to discuss the use of the SEM in this section. Evidence of the incorporated impurity was found by operating the SEM in the X-ray fluorescence (XRF) mode. However, the sensitivity was such that the impurity could only just be seen above the background. Figures 4a and b demonstrate this situation. It was not possible to obtain useful information on contact homogeneity as was originally hoped.

5. ALTERNATIVE TECHNIQUES

There are several other analytical techniques which can be used to examine laser-doped contacts. These include transmission electron microscopy (TEM), secondary ion mass spectrometry (SIMS) and low energy electron diffraction (LEED). These techniques have already been used in other laboratories to examine, in the main, the annealing of ion-implanted materials.

Nuclear reaction analyses may also be useful to profile low mass impurities in higher mass substrates: for example, Li in Ge and Si. The reaction ^{7}Li (p, α)^{4}He is being considered but no experimental data have yet been collected.

Deep level transient spectroscopy (DLTS) may prove useful in examining the radiation damage defects and associated complexes produced by pulsed laser irradiation.

Improvements to present techniques would allow more detailed information to be obtained. For example, stripping methods permit the contact electrical activity to be profiled. Better control and more accurate knowledge of the laser energy, and also of the thickness of the evaporated dopant layer, are necessary to determine the parameters necessary to produce good blocking contacts.

6. SUMMARY AND CONCLUSIONS

Evidence for surface melting and electrical activity was easily obtained with the optical microscope and the thermal probe. Blocking and ohmic contacts were readily made by laser doping, although in many cases the quality of the blocking contact was inferior to those produced by more conventional means. The reasons for this are not properly understood at present but excess laser energy is suspected.

To identify the dopant and estimate the contact thickness requires a more sophisticated technique. SEM (XRF) was considered but found to be too insensitive. On the other hand, RBS was suitable, although there is a lower mass limit. The sensitivity seems to be adequate and, in general, the mass and depth resolutions are quite acceptable. By operating a nuclear radiation detector with a laser-doped contact, it was confirmed that, qualitatively, the contacts are thin.

Although electrical activity could be inferred from RBS measurements when a substitutional component was found, more direct evidence was obtained by making sheet Hall measurements which provided (sheet) resistivities and carrier concentrations.

In conclusion, it has been demonstrated that thin, heavily-doped contacts can be formed on semiconductors by pulsed laser irradiation of thin surface dopant layers. Reasonable agreement was found between the two methods of measuring electrical activity. Substitutional solubilities well above the equilibrium values were observed for In and Sb in Si and Ge.

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NOTES

TABLE 1

LASER DOPING OF Ge AND Si

Dopant/Type		Ge	Si
Ga	p	Vacuum evaporated layer	Vacuum evaporated layer
In	p		
Al	p		
Sb	n		
As	n	Not attempted	Not attempted
B	p		

TABLE 2

SHEET HALL AND RESISTIVITY MEASUREMENTS ON LASER-DOPED GERMANIUM

Sample/Dopant		ρ_s (Ω/□)	N_s (cm^{-2})	μ_{eff} ($cm^2 s^{-1} V^{-1}$)
Ge	Ga	6.4	3.7×10^{14}	2.6×10^3
Ge	Sb	1.9 x 10	2.3×10^{15}	1.4×10^2
Ge	In	3.8 x 10	3.3×10^{15}	5.0 x 10

TABLE 3

LINEARITY OF LASER-DOPED Sn CONTACTS ON n-GaAs

Sample	Current Range Examined (A)	Correlation Coeff.	V Cut-off (V)
73-3A	1×10^{-6} - 2×10^{-2}	0.997	0.3
LPE 73-7	3×10^{-6} - 2×10^{-3}	0.997	1.0
MCP #1	3×10^{-6} - 5×10^{-3}	0.998	0.65
MCP #2	1×10^{-6} - 3×10^{-3}	0.999	0.7

TABLE 4

TYPICAL DATA FROM RBS SPECTRA

Substrate	Impurity	RANDOM FWHM nm	RANDOM Conc. atom %	CHANNELLED FWHM nm	CHANNELLED Conc. atom %	χ_{min}.%
Ge	In	93	1.7	74.0	0.7	7.4
Ge	Sb	109	23.4	96	22.3	4.5
Ge	-					3.5
Si	Ga	69	1.0	76	0.4	3.3
Si	-					3.0
GaAs	Sn	52	0.8	40	0.4	8.2
GaAs	-					4.5

TABLE 5

COMPARISON OF THE ELECTRICALLY ACTIVE IMPURITY CONCENTRATIONS OBTAINED FROM RBS AND SHEET HALL MEASUREMENTS

Substrate	Impurity	Conc. atom %	FWHM nm	Conc. atom cm^{-2}	Sheet Hall Conc. atom cm^{-2}
Ge	In + a-Ge*	1.2	151	8.0×10^{15}	5.0×10^{15}
Ge	Sb	1.4	43	2.6×10^{15}	1.8×10^{15}
Si	Ga	0.6	69	2.0×10^{15}	4.4×10^{15}

*a-Ge indicates that an additional layer of Ge was evaporated

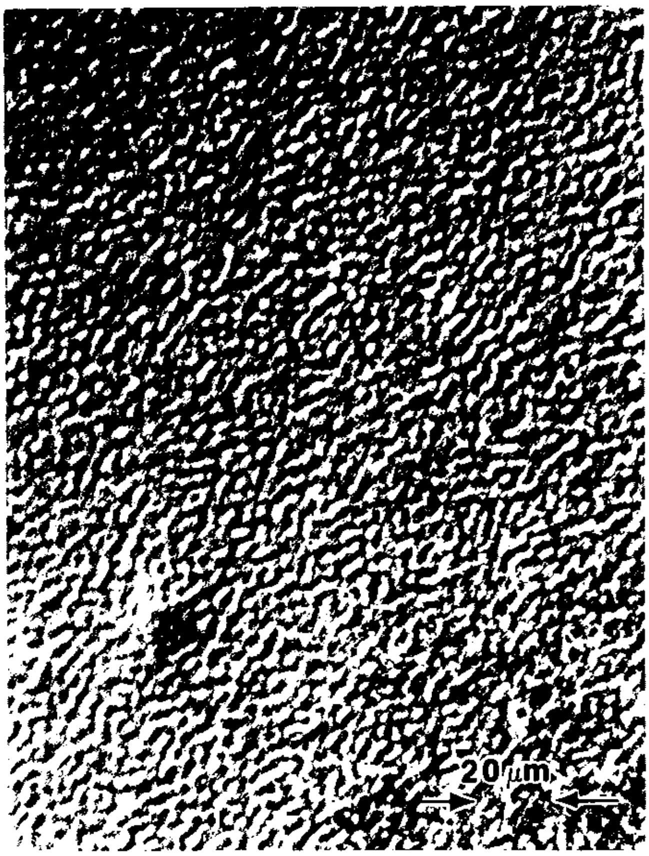


FIGURE 1. THE SLIGHTLY EXAGGERATED 'ORANGE PEEL' FINISH FOUND ON AN Si SAMPLE AFTER PULSED LASER IRRADIATION

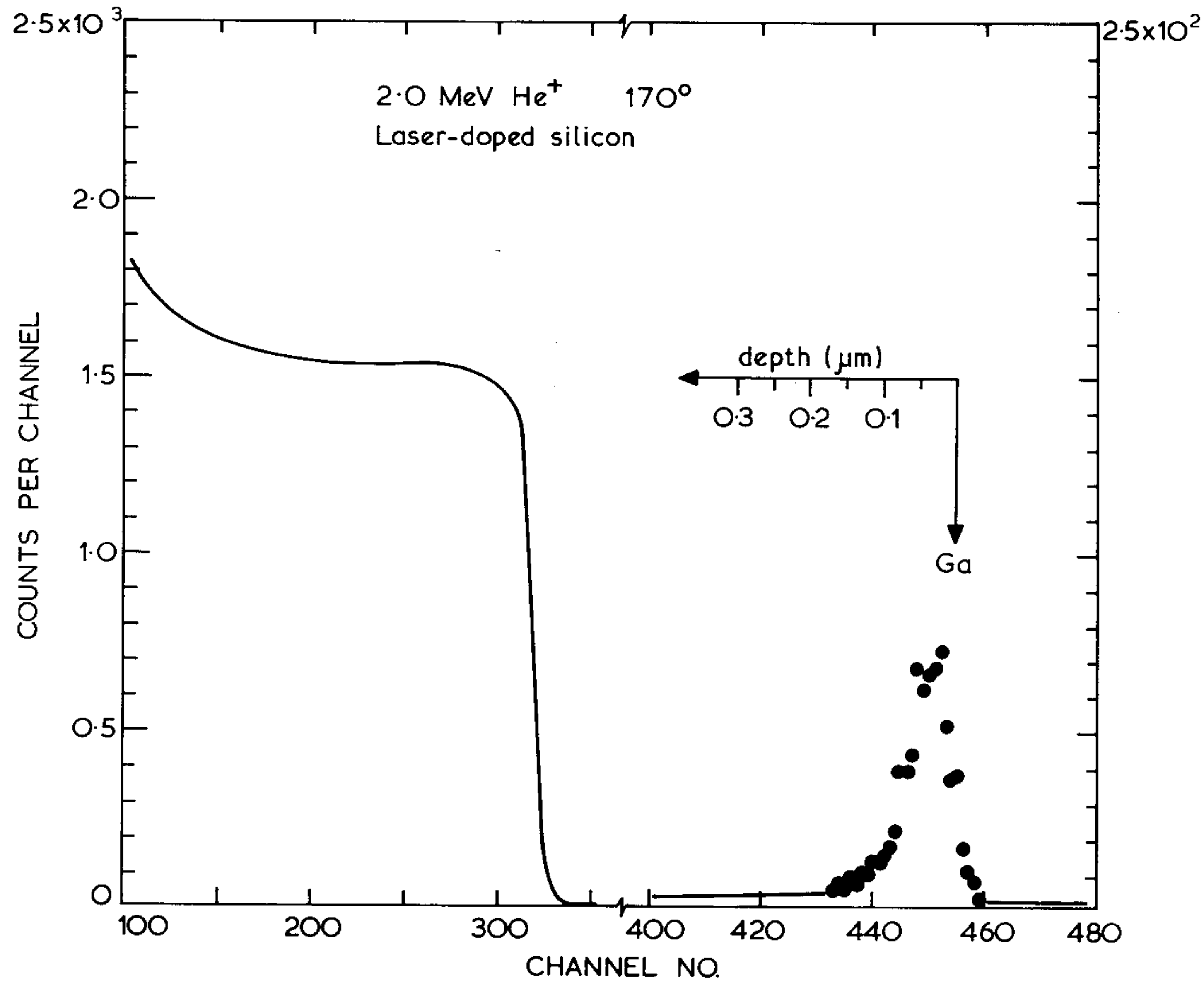


FIGURE 2. A RUTHERFORD BACKSCATTERING RANDOM SPECTRUM SHOWING THAT Ga HAS BEEN MIXED INTO THE SURFACE OF AN Si SAMPLE

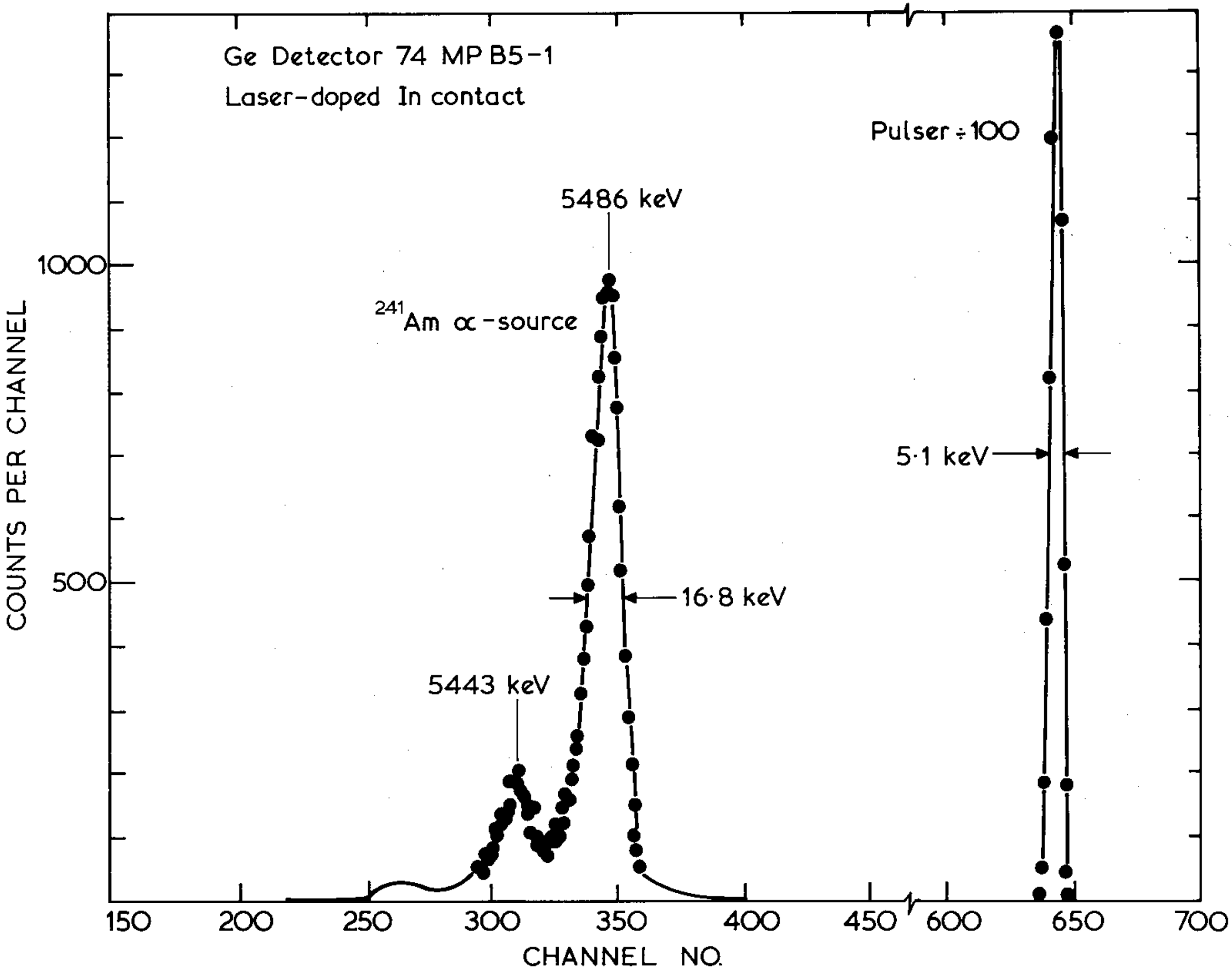
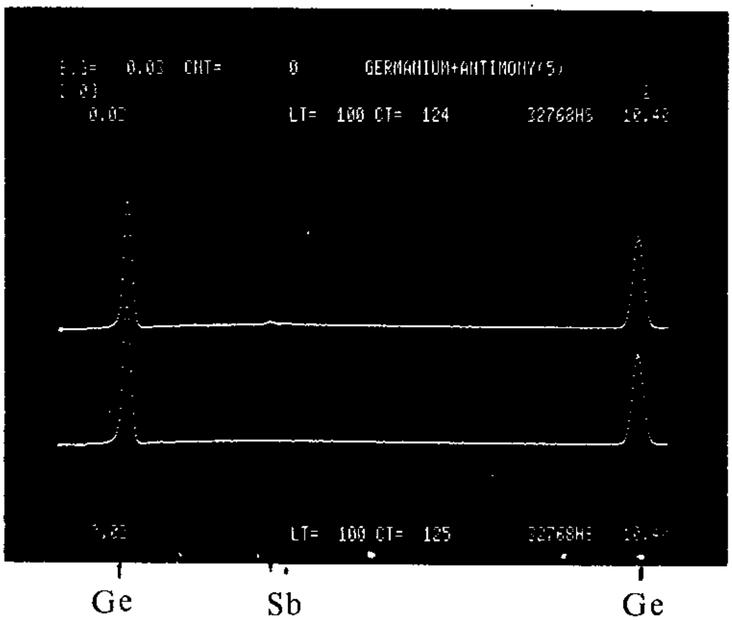
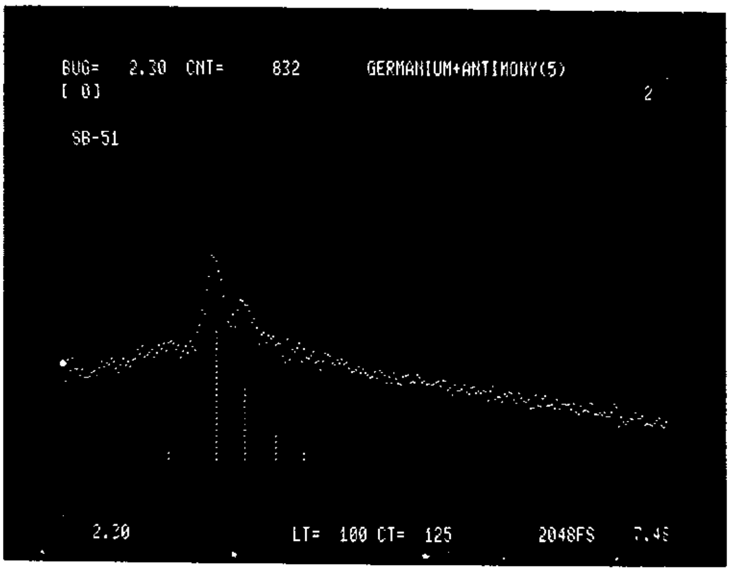


FIGURE 3. AMERICIUM-241 PARTICLE SPECTRUM RECORDED BY A Ge DETECTOR (77 K) HAVING A LASER-DOPED FRONT CONTACT



(a) The upper trace was recorded from the laser-doped spot. The Sb X-rays can be seen just above the background. The lower trace was taken on bare undoped Ge.



(b) Detail of the Sb X-ray region. The markers indicate the positions of the L X-rays. Marker lengths indicate relative intensities.

FIGURE 4. SPECTRA RECORDED ON A Ge SAMPLE LASER-DOPED WITH Sb, USING AN SEM IN THE XRF MODE