Growth and Applications of Epitaxial $Si_{1-x}Ge_x$ Alloys Grown by Rapid Thermal Chemical Vapor Deposition

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ABSTRACT

This paper describes the growth of epitaxial $Si_{1-x}Ge_x$ layers on silicon by Rapid Thermal Chemical Vapor Deposition as a path towards the development of silicon-based heterojunction integrated circuits. The basic physics and performance of heterojunction bipolar transistors in this material system is reviewed, and the results of photoluminescence experiments in the strained layer alloys are also presented.

INTRODUCTION

Since the beginning of the integrated circuit era some thirty years ago, silicon integrated circuits have expanded to the level of now containing over 10,000,000 transistors per chip. While the materials of which the IC's consist now includes silicon nitride, silicon dioxide, metal silicides, polyimides, aluminum and various aluminum alloys, the actual semiconductor crystal which comprises the heart of the transistors has remained silicon. Silicon has not been chosen because of its optimal electrical properties, etc., but rather because of its excellent material processing capabilities. For example, stable insulating oxides which also serve as diffusion barriers are easily formed on its surface, crystal damage from ion implantation is easily repaired by annealing, large diameter dislocation-free wafers are readily produced, etc.

It has long been recognized however, that far superior electrical performance com-

pared to all silicon "homojunction" devices might be realized if one could fabricate different parts of a transistor out of semiconductors with different bandgaps. A major roadblock towards achieving such "heterojunction" transistors has been the problem of growing one compatible semiconductor on top of another without a large number of defects at the interface or in the top film. For example, while spectacular results have been achieved by using combinations of GaAs and $Al_{1-x}Ga_xAs$ in devices in the past decade, these results have not been transferable to silicon integrated circuit technology for two reasons. First, these compounds and most other III-V semiconductors are not compatible with silicon processing techniques; at high temperatures these semiconductors can decompose and their constituents can dope the silicon. Second, although their basic crystal structures are similar (diamond-like vs. zincblende), the lattice constants of GaAs and $Al_{1-x}Ga_xAs$ are substantially larger than that of Si (~4%), making it difficult to grow one on top of the other. Unfortunately, no compatible semiconductor "lattice-matched" to silicon exists.

A breakthrough occured in the 1970's and early 1980's when it was found that alloys of silicon and germanium ($Si_{1-x}Ge_x$) could be grown, within limits, lattice-matched to silicon substrates [1-4]. Although the films were in biaxial compression since the natural relaxed lattice constant of these alloys is greater than that of silicon [5], for thin films this is the preferred growth mode. For such thin films the energy saved by growing commensurate to the substrate to avoid misfit dislocations is larger than the compression energy of the film. Such films are technologically attractive for several reasons. First the $Si_{1-x}Ge_x$ material system is much more compatible with silicon processing than GaAs, eg., since Ge and Si do not serve as dopants in each other. Since Ge has bandgap smaller than silicon, the bandgap of the alloys can be adjusted by controlling the germanium fraction x. Furthermore, the strain serves to split band edge degeneracies, further reduc-

ing the bandgap so that a $Si_{0.8}Ge_{0.2}$ layer has a bandgap ~160 meV less than that of silicon [6,7]. Therefore there now exists a basic material system for developing heterojunction transistors and other heterojunction structures on a silicon-based material system for integrated circuits. For further information on the basic electrical and mechanical properties of $Si_{1-x}Ge_x$ strained alloys on silicon, the reader is referred to Ref's 1-4 and 6-7 as a good introduction.

The initial growth experiments of $Si_{1-x}Ge_x$ alloys described above were performed by Molecular Beam Epitaxy (MBE). This UHV evaporation technique is well suited for research applications because of its flexibility and control, but it is not well suited for manufacturing. Chemical Vapor Deposition (CVD), because of its easily renewable gas sources and ability to scale to larger sizes, is a preferred thin film growth technology for industrial applications. Two alternative CVD approaches have emerged over the past several years. One involves processing an entire boat of wafers at once in a UHV furnace environment (UHV-CVD) [8]. The other generally involves only a single wafer at a time, but the wafer temperature can be varied rapidly by external lamp heating. Such Rapid Thermal Chemical Vapor Deposition (RTCVD) and its application towards devices such as heterojunction bipolar transistors and optical emitters is the focus of this article.

GROWTH OF $Si_{1-x}Ge_x$ ALLOYS BY RAPID THERMAL CHEMICAL VAPOR DEPOSITION

The central feature of a RTCVD reactor is a growth chamber which consists of a quartz tube (or steel with quartz windows) so that the wafer may be heated by radiation from a high intensity lamp bank outside of the reactor (Fig. 1). To enable rapid changes in the sample temperature, the wafer is typically supported on quartz pins without a susceptor. Although a horizontal gas flow is shown in Fig.1, vertical or annular flows are also used.

Not shown in Fig.1 is the gas manifold and supply system or the pumping apparatus. Typical growth conditions in such a system are a gas flow of 1 % dichlorosilane in a hydrogen carrier at 6 torr. Silicon is typically grown from ~700°C (40 Å /min) to 1000°C (0.25 μm/min). Germane is added to provide a germanium source for the alloy growth, and the films are often grown at 600 - 650 °C as described below. The growth rates can still be fairly high (>100 Å /min), however, because of a catalytic reaction of the germane on the silicon growth rate [9,10].

The first silicon epitaxial growth experiments in a reactor like that of Fig. 1 were performed by Gibbons et al [11] and were termed Limited Reaction Processing (LRP). The central feature of LRP is that the reactive gas flows were first established when the reactor was cold, and then the growth reaction was switched on and off using rapid changes in sample temperature (up to 300 K/s). This differs from the conventional CVD approach where the wafer is first brought to the growth temperature in a passive ambient (i.e. hydrogen) before the reactive gas flows for growth are introduced. In both approaches the growth conditions such as temperature can be optimized for each individual layer in a multi-layer structure. In LRP, the gases can be switched while the wafer is cold, and subsequent temperature pulses can be changed for each layer. In the conventional approach, the reactive gas flows can be turned off while the wafer temperature is directly ramped from that for one layer to that for the next.

The relative merits of the two approaches for structures on a 100-Å scale can be examined by considering a p-i-p-i superlattice with 100-Å layers (Fig. 2). At 1000 °C, typical growth rates are on the order of 0.25 μm/min, so each 100 Å layer requires only 2.4 sec at the growth temperature. Diffusion constants are so high at this temperature that even the simulated profile grown by LRP to minimize diffusion already has interfaces seriously degraded on a 100-Å scale. This shows that at high temperature growth

absolute minimization of the time at the growth temperature is important, but still not sufficient for 100-Å structures. At lower temperatures, longer growth times are required because of slower growth rates, but because the activation energies of growth are smaller than those of typical substitutional diffusers (2 vs. 3-5 eV), more abrupt structures can be grown, as demonstrated by the 800 °C simulation in Fig. 2 [12]. At temperatures under 800 °C, the times for 100 Å layers will be on the order of one minute, so that the several seconds savings of thermal exposure made possible by LRP may not be significant. The gas switching approach also has the potential advantages under these conditions that control of rapid temperature ramps is not required. Using the gas-switching approach, well-resolved $Si/Si_{1-x}Ge_x$ superlattices have been grown with periods as small as 45 Å (Fig. 3) [12].

The previous discussion indicated that temperatures under 800 °C are required for the growth of 100 Å structures. For $Si_{1-x}Ge_x$ strained layers, even lower temperatures (<650 °C) are needed to achieve metastable strained layers in excess of critical thickness and to prevent non-planar growth modes [3]. At low temperatures, however, silicon-based CVD growth becomes exceedingly difficult because of the enhanced stability of oxygen and water on the silicon surface [13,14]. The first successful silicon epitaxial experiments in the 600 °C range were performed by UHV-CVD [8]; the low gas pressures (mtorr) resulted in a very low partial pressure of any impurities (such as water vapor) that might be contained in the gas source. Initial epitaxial experiments in this range by RTCVD were performed in a reactor without a load-lock, so that the reactor chamber was vented to atmosphere each time a sample was loaded. The resulting oxygen levels in $Si_{1-x}Ge_x$ films grown at 640 °C were $10^{20} cm^{-3}$ [15], two orders of magnitude higher than is generally acceptable in silicon films. Subsequent experiments using a load-lock to reduce water and oxygen levels showed that high-lifetime low-oxygen films could indeed

be grown in a non-UHV RTCVD reactor at 625 °C [16]. This trend has actually been continued through improved gas purity and reactor design to the point where low oxygen films can now be grown in this temperature range at atmospheric pressure [17].

HETEROJUNCTION BIPOLAR TRANSISTORS

The heterojunction bipolar transistor (HBT) is a device which benefits exponentially from small changes in the bandgap within the device structure. The basic device consists of three semiconductor layers known as the collector, base, and emitter collectively. The principle of the HBT is shown in Fig. 4 which shows the location of the conduction and valence bands of the semiconductor vs. distance for both an all silicon homojunction transistor and for a narrow bandgap base HBT device where the base is made of $Si_{1-x}Ge_x$ and the emitter and collector regions are made of silicon. Under normal bias conditions, electrons in the conduction band travel from the emitter over the base barrier to the collector to form collector current (I_C). Holes also travel in the valence band from the base to the emitter to form base current (I_B). Since the current gain is I_C/I_B, large collector currents and small base currents are desirable. If bandgap of the base region is reduced and the base doping is held constant (which keeps the valence band in the base at approximately the same level), it is clear that electrons (which travel in the conduction band) will face a lower barrier as they travel from emitter to collector. To first order, the resulting increase in I_C will be by a factor of $e^{\Delta E_G/kT}$, where ΔE_G is the bandgap reduction. Furthermore, since the barrier faced by holes is unchanged, the base currents should be unchanged, resulting in an increased gain by the same factor. For example, for a $Si_{0.8}Ge_{0.2}$ base, the bandgap reduction of ~160 meV results in approximately a 500-fold increase in I_C at room temperature. This extra gain itself may be useful for an improved circuit, or the base doping could then be increased to reduce the base

resistance. Increasing the base doping brings the gain back down, but high base resistance a serious parasitic that often limits circuit performance more than the gain of the transistor.

The first $Si/Si_{1-x}Ge_x/Si$ HBT's grown by any technique that exhibited a near-ideal exponential increase in collector current were grown by LRP[15], but base currents were excessively large and limited the gain of the devices. Subsequent results in films grown by UHV-CVD or RTCVD with low oxygen levels have confirmed that ideally-low base currents which are independent of the base composition are also possible [18,19] in addition to the increased collector currents. An example of the effect of the narrow bandgap base on performance is shown in Fig. 5, where an all silicon device and a device with a base of $Si_{0.86}Ge_{0.14}$ but otherwise similar dopings are compared. The gain increases from 6 to 700 as expected with the narrow bandgap base. A related advantage of the HBT's is the possibility of low temperature operation. The gain of conventional bipolar transistors actually degrades at low temperature because of bandgap narrowing due to the heavy doping normally present in the emitter (resulting in an HBT but with the bandgap reduced on the wrong side of the emitter-base junction). This can be more than compensated for in the narrow bandgap base HBT's, and the effect should become larger at low temperature when kT is reduced. For example, the gain of an all silicon bipolar transistor typically decreases from 100 to <10 as the temperature is lowered from 300K to 100K, but the gain of an HBT with a $Si_{0.8}Ge_{0.2}$ base has been observed to increase from 1000 to over 10,000 over the same temperature range [19].

Besides the possibility of increased gain (or lower base resistance), a second advantage of HBT's is the possibility introducing a "built-in" electric field in the base by grading the germanium content (and thus the bandgap) across the base region. This electric field can speed up the electrons as they travel across the base, resulting in a higher speed

device. Researchers at IBM have recently demonstrated $Si/Si_{1-x}Ge_x/Si$ HBT's with such grade bases which exhibit current gain at frequencies up to 75 GHz at room temperature and 96 GHz at low temperature [20,21]. These devices were actually grown by UHV-CVD, but devices with similar grading have been grown by RTCVD as well [19]. In both cases the grading was accomplished by adjusting the source gas flows as a function of time. These speed results represent over a 60% increase over previous silicon-based device speeds, and open up a new frequency performance regime to silicon integrated circuits.

PHOTOLUMINESCENCE SPECTRA

A long sought goal of microelectronics has been a material technology for monolithically integrating the worlds of optoelectronics and VLSI technology. This is a difficult challenge since optoelectronics is based on III-V semiconductors such as GaAs and InP with direct bandgaps, and VLSI is based on silicon because of its manufacturability. One then faces the incompatibility and lattice mismatch problems described earlier in this paper. Although $Si_{1-x}Ge_x$ alloys are still indirect bandgap materials, it has been predicted that certain short period Si/Ge superlattice structures will exhibit "zone-folding" effects which will create a pseudo-direct gap material from the indirect bandgap constituents, and hence have the possibility of emitting large amounts of light [22,23]. The simplest experimental probe of a semiconductor structure for its light-emitting properties is photoluminescence (PL) -- light is shined on the semiconductor to create electron-hole pairs, and one observes the spectrum of light that is emitted as the electrons and holes recombine. The PL results from such zone-folded structures [24, 25] are at present somewhat controversial [26], however, especially since some of the signals seen closely correspond to the known dislocation photoluminescence in silicon. Other MBE work has produced single strained films which have a strikingly large PL efficiency (10%)

[27]. The signal is very broad (~80 meV) and substantially below the bandgap (~ 120 meV), however, and the exact transition which causes this emission is not known.

The photoluminescence spectra of $Si_{1-x}Ge_x$ strained layers, quantum wells, and superlattices grown by RTCVD [28] has proved to be substantially different from those earlier reported by MBE. Typical spectra of a sample with multiple $Si/Si_{0.8}Ge_{0.2}/Si$ quantum wells measured at 2K and 77K are shown in Fig 6. In the 2K spectra one sees several well-resolved peaks which can be identified by comparison to the comprehensive work of Weber and Alonso [29] on bulk *unstrained* $Si_{1-x}Ge_x$ alloys. The large high energy peak is from direct recombination of electrons and holes without a phonon, and the other lower energy peaks (TA and TO) are the recombination of the same electron and holes but accompanied by the emission of a phonon (TA or TO), so that the energy of the emitted photon is lower by the energy of the phonon. Note that the TO phonon, which represents a local mode vibration, actually splits from a single peak in silicon to three peaks in the alloy. This is because there are three possibilities for nearest neighbors (Si-Si, Si-Ge, and Ge-Ge). A very interesting feature is the no-phonon (NP) recombination signal. Such a signal is commonly observed in silicon at low temperature when the excitons are bound to localization sites, but not at higher temperatures (over 20K) when the excitons are free. In the $Si_{1-x}Ge_x$ alloys grown by RTCVD, the NP signal actually does persist to higher temperatures when the excitons are no longer bound [28]. This NP peak is still clearly evident (although thermally broadened) at 77K (Fig. 6) and has been observed up to 300K. The physical basis for such no-phonon luminescence in an indirect gap material lies in the fact that the $Si_{1-x}Ge_x$ is a *random* alloy. The randomness of the material breaks the perfect translational symmetry of the lattice -- the arrangement of neighbors looks different from each lattice site. Therefore the usual Bloch wavefunctions, which are eigenstates of momentum k, are no longer the eigenstates

of the electrons in the crystal. The true eigenstates can be found by perturbation theory, which will mix different k-components into each state. Therefore nearly any two electron and hole wavefunctions will have some optical matrix element between them, and optical transitions without phonons are allowed. A similar effect was observed in the relaxed $Si_{1-x}Ge_x$ alloys as well [29]. It should be stressed however that zone-folding and pseudo-direct bandgap effects are not being observed, since the superlattice periods are too big (>40 Å) and similar signals are observed in single $Si_{1-x}Ge_x$ films as well as the superlattices.

That such well-resolved bandedge photoluminescence is observed in the RTCVD films is a reflection of their high material quality. First, the high lifetimes in the RTCVD films means that the non-radiative recombination from defect sites was low enough so that the carrier could radiatively recombine to give rise to a PL signal. This may be why such a signal was not previously observed in films grown by other techniques. Further, the narrow linewidth of the signal (FWHM of 5 meV of the NP signal at 2K) is comparable to the best ever reported for relaxed bulk alloys, indicating the good uniformity of the alloys and an absence of significant clustering. The well resolved PL should be a useful tool for studying the band structure of the alloys. For example, the only previous direct measurement of the bandgap of $Si_{1-x}Ge_x$ strained alloys was performed by photocurrent spectroscopy [7], where the photocurrent generated in a p-i-n diode was measured as a function of wavelength. The relation of the optical absorption edge measured in those experiments to the true bandgap is somewhat uncertain, however, since one must know the energies of any phonons, if any, emitted as part of the absorption process. Since the NP PL transition provides a direct measure of the alloy bandgap, it should be possible to directly measure the alloy bandgap as a function of composition, without uncertainty due to phonon effects.

CONCLUSIONS

Rapid Thermal Chemical Vapor Deposition is a competing technology for the growth of $Si_{1-x}Ge_x$ strained layer structures for the development of silicon-based heterojunctions. High quality epitaxial films with growth temperatures as low as 600 °C and 45-Å period superlattices have been demonstrated without the use of ultra-high vacuum techniques. $Si/Si_{1-x}Ge_x/Si$ narrow bandgap base heterojunction bipolar transistors have been shown to have superior characteristics compared to all silicon homojunction devices, and extend the scaling limits of bipolar transistors. Finally, RTCVD strained $Si_{1-x}Ge_x$ films exhibit well resolved band-edge photoluminescence, the first step on the way to developing silicon-based light-emitting devices.

ACKNOWLEDGEMENTS

The $Si_{1-x}Ge_x$ research effort at Princeton has been supported by the Office of Naval Research, the National Science Foundation and the NJ Comm. on Science and Tech. The author would also like to thank C. Magee (Evans East), S. Schwarz and B. Wilkens (Bellcore), E. Fitzgerald (ATT), L. Lenchyshyn and M.L.W. Thewalt (Simon Fraser University), and N. Rowell, J.P. Noel, J. McCaffrey, and D.C. Houghton (National Research Council, Canada) for their contributions and collaborations on various parts of the work at Princeton. Finally, the author would like to acknowledge P.M. Garone, H. Manoharan, E.J. Prinz, C.M. Reaves, P.V. Schwartz, and X. Xiao for their work at Princeton.

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Figure Captions

Fig. 1. Schematic view of a RTCVD apparatus.

Fig. 2. Simulated profile of a p-i-p-i superlattice grown at 1000 °C and at 800 °C with no excess thermal exposure [12].

Fig. 3. Cross section TEM of a $Si/Si_{0.8}Ge_{0.2}$ 50-period superlattice grown by RTCVD with a period of 45 Å [12].

Fig. 4. Band diagram showing collector and base current components in a homojunction transistor and a HBT.

Fig. 5. Common-emitter characteristics of (a.) an all silicon bipolar transistor and (b.) a $Si/Si_{0.86}Ge_{0.14}/Si$ device with similar doping levels.

Fig. 6. Comparison of 4K (a) and 77K (b) photoluminescence spectra for a sample consisting of multiple $Si/Si_{0.8}Ge_{0.2}/Si$ quantum wells.

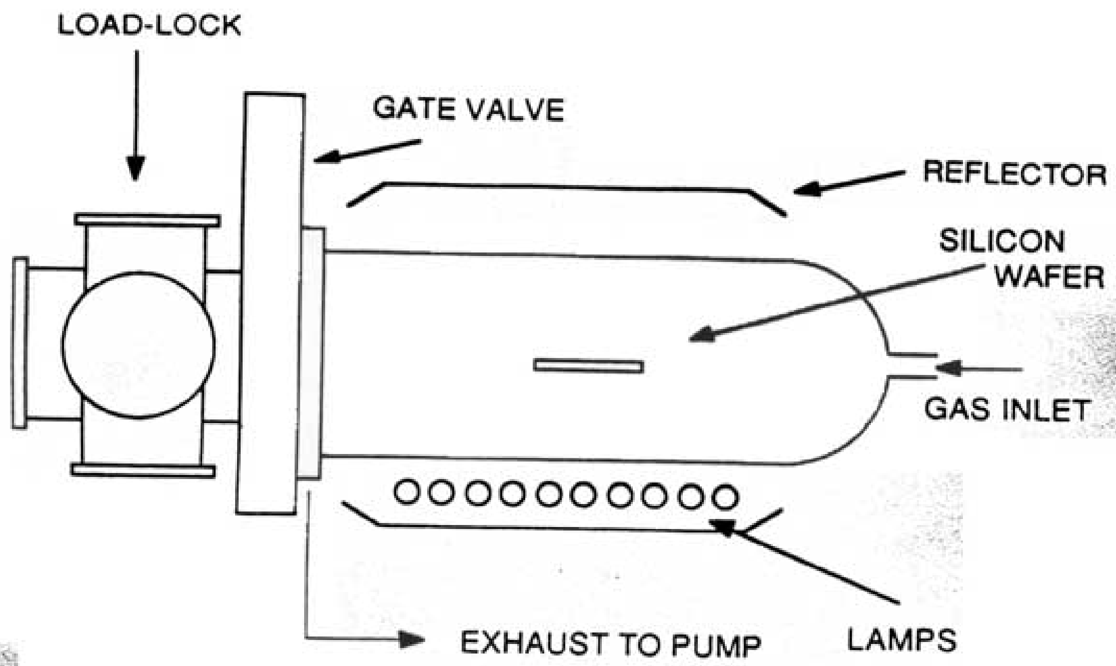

Fig 1

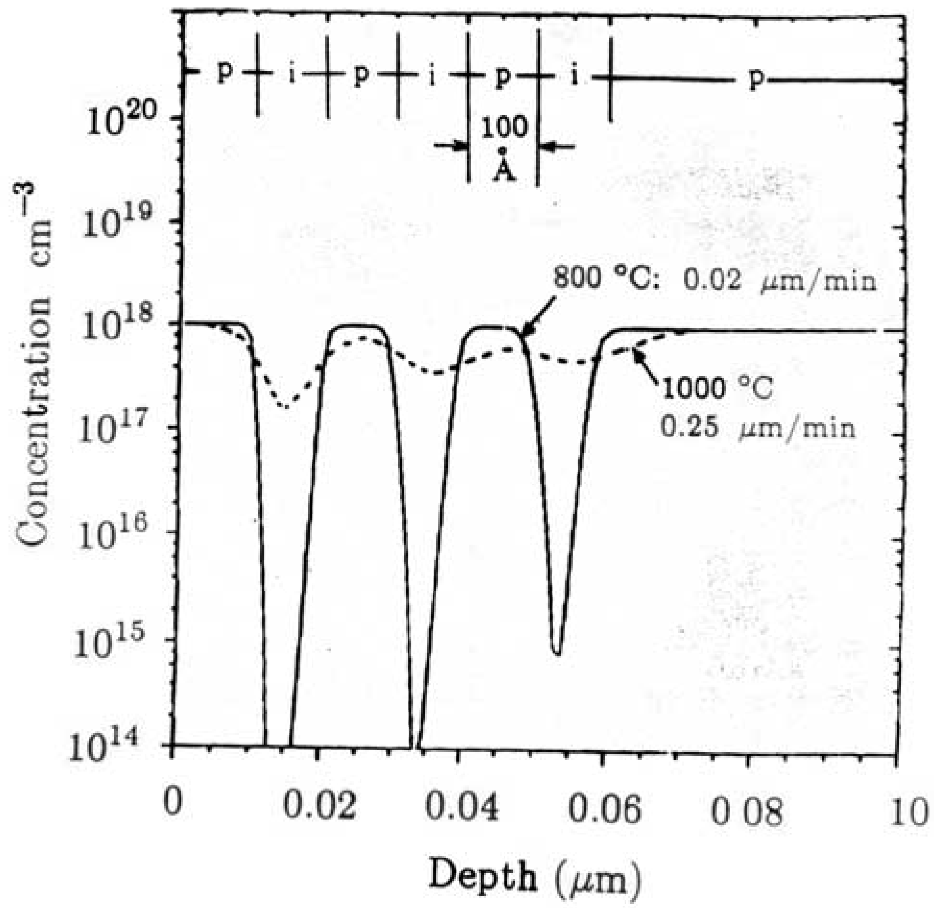

FIG 2

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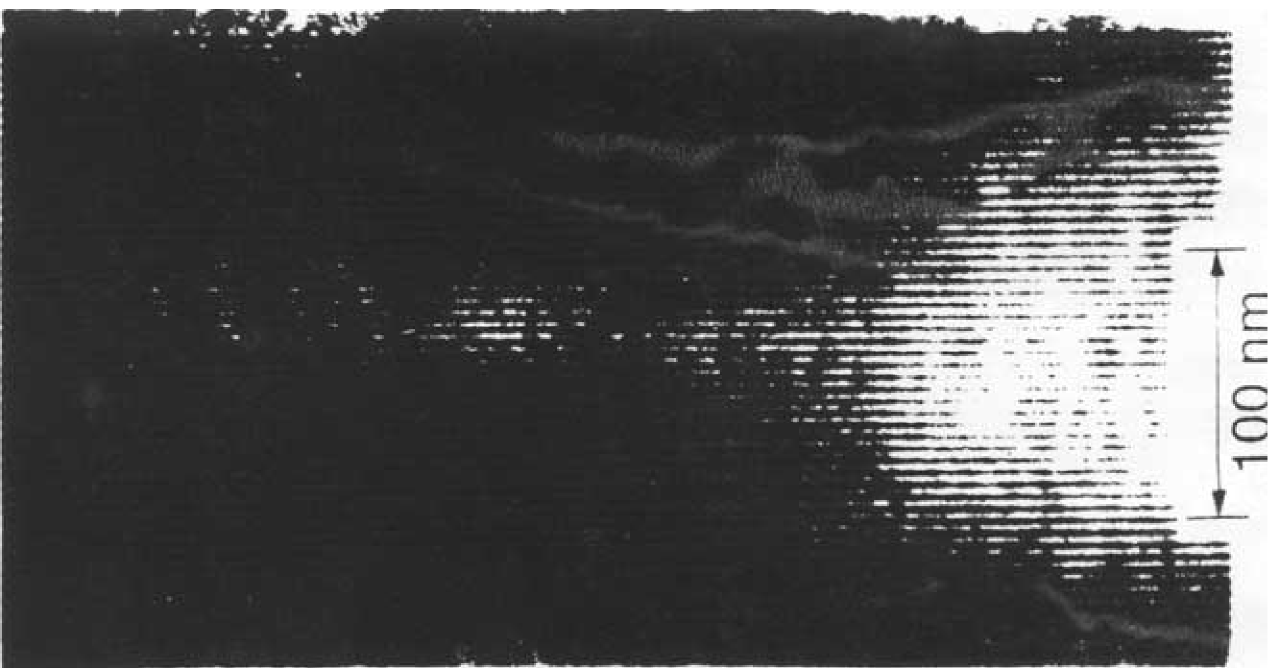


F 3

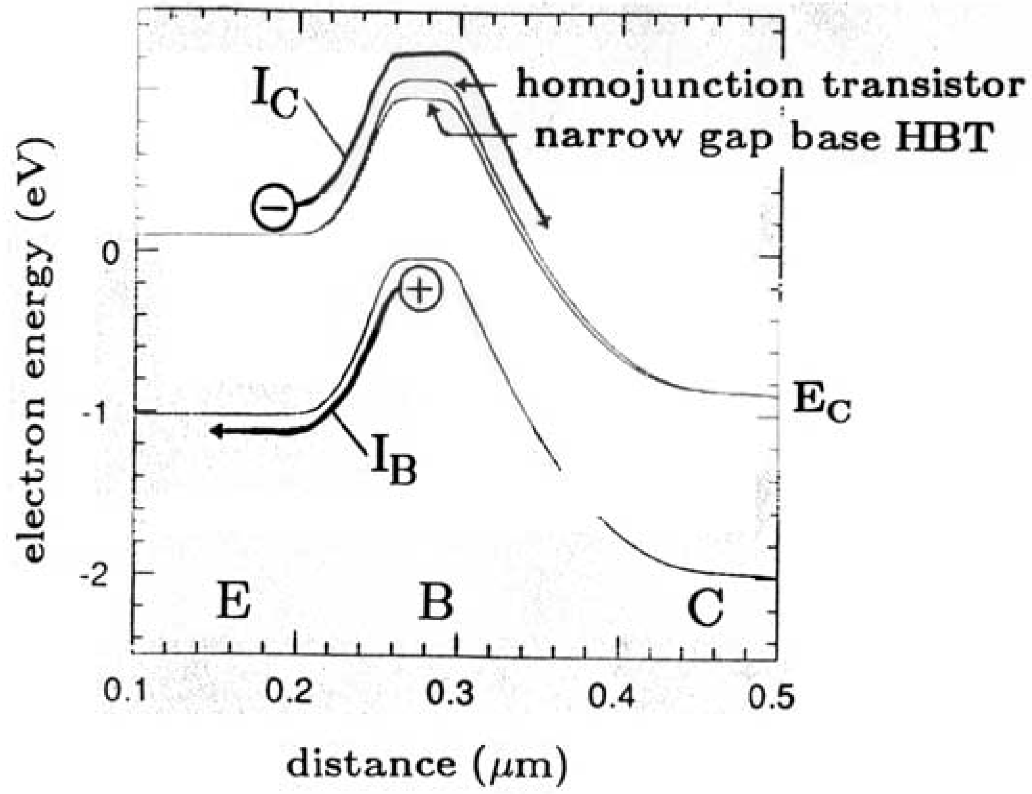
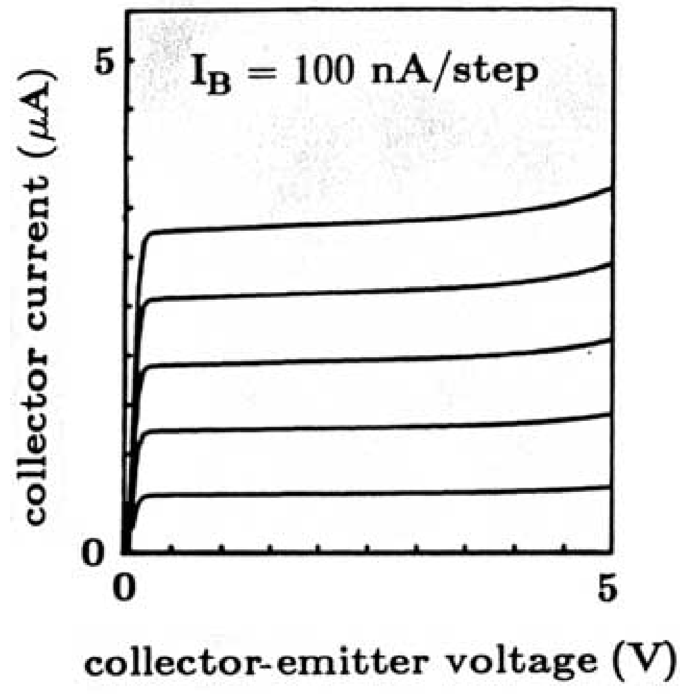


FIG 4



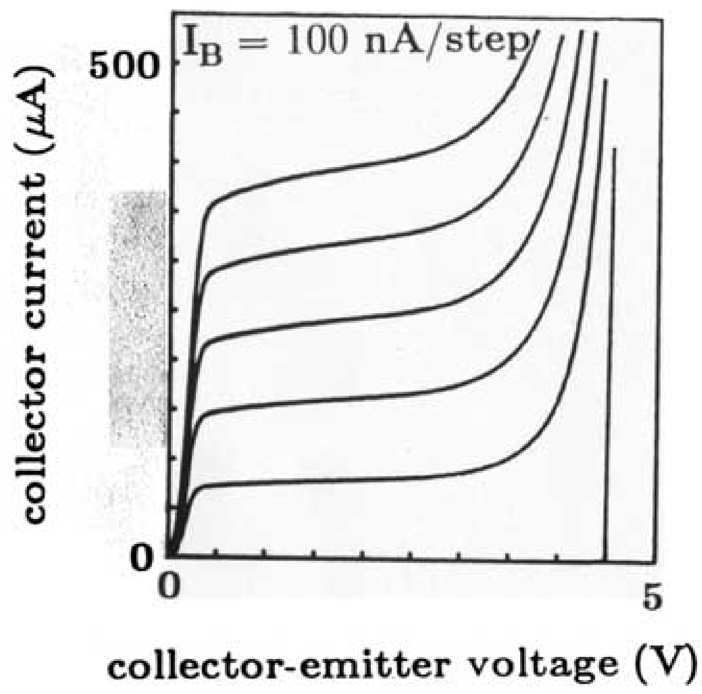
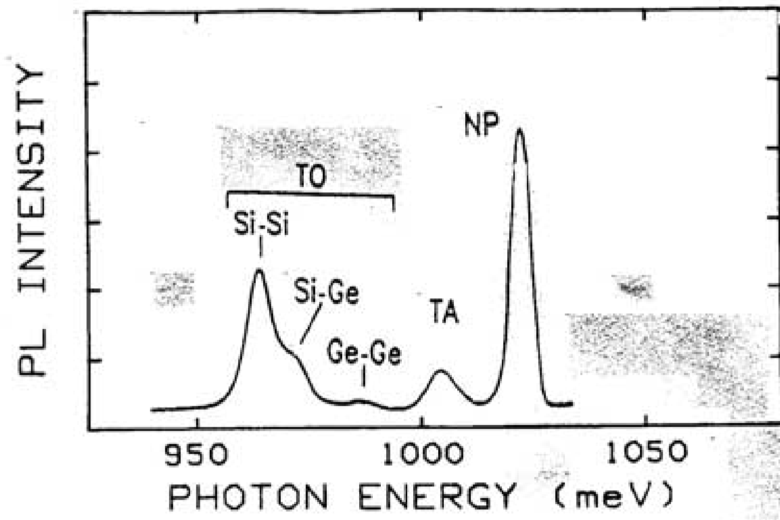
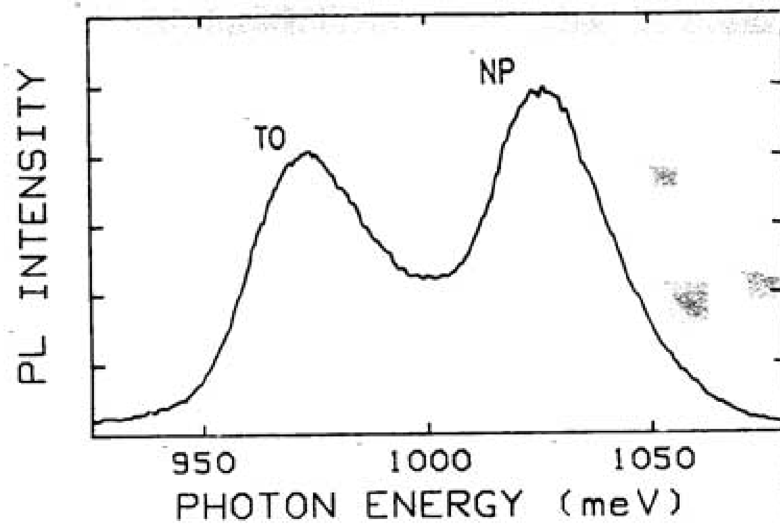


FIG 5



(a)



(b)

FIG 6