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Development of Ultra Pure Germanium Epi Layers for Blocked Impurity Band Far Infrared Detectors

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**Development of Ultra Pure Germanium Epi Layers
for Blocked Impurity Band Far Infrared Detectors**

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1. INTRODUCTION

The desire of astronomers and astrophysicists to study infrared radiation from the far universe, in order to learn about star birth, infrared galaxies, the density of matter as a function of distance, etc., has led to the development of a number of advanced detectors for the infrared. Extrinsic germanium (Ge) far-infrared radiation detectors respond to photons whose wavelengths lie in the range 15–250 μm . Extrinsic germanium infrared detectors were used very successfully on the Infrared Astronomy Satellite (IRAS) [1], and current plans for the Space Infrared Telescope Facility (SIRTIF) have led to continued interest in highly-sensitive far-infrared Ge photoconductors.

Conventional gallium-doped germanium detectors respond to wavelengths below 120 μm [2], whereas stressed gallium-doped germanium detectors (see Fig. 1) respond to wavelengths below 250 μm [3]. The effect of applying uniaxial stress along the (100) axis of a Ge:Ga crystal is to split the degeneracy of the valence band, and to reduce the ionization energy of the Ga acceptor states. This shifts the onset of photoconductivity to longer wavelengths. The wavelength of the photoconductive onset increases with higher levels of stress. This has led to the development of compact housings that allow the application of stress up to the point of fracture, which is approximately 1000 N/mm². Stressed detectors are difficult to make into arrays, because of the mechanical housing used to apply the stress. This makes the realization of one-dimensional and (especially) two-dimensional arrays inherently difficult. It is hoped that germanium blocked impurity band (BIB) detectors, which do not need any external stress-applying apparatus, and therefore can more easily be made into one- and two-dimensional arrays, will exhibit long-wavelength response similar to that of stressed detectors [4,5].

BIB detectors have two other desirable characteristics. One is the small detector volume, which lessens the probability of interference from cosmic radiation,

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Fig. 1. Measured spectral responsivity of a conventional and stressed Ge:Ga detector [2].

without decreasing the output signal of the detector. The other is the reduction of noise in BIB detectors, which is due to the unity gain.

It has been shown that silicon BIB detectors made by Rockwell International do meet their expected device specifications [6,7,8]. Consequently, there has been much interest in applying this concept to germanium.

Germanium BIB detectors were fabricated by Rossington, and are described in her thesis [9]. Rossington's BIB detectors employed a pure Ge epitaxial layer on a heavily-doped substrate. The epitaxial layer was grown using atmospheric pressure chemical vapor deposition (CVD). The detector characteristics, i.e., dark currents, responsivity, and NEP, were not optimal, hence further research in this area was warranted. Ge:Ga BIBs fabricated by Rockwell International exhibited long-wavelength thresholds of 190 μm , and peak quantum efficiencies of 4% [5], but large leakage currents.

The main goals of my project were:

- (1) To develop a low-pressure CVD (LPCVD) process that allows epitaxial growth at lower temperatures. Lower temperatures will allow the achievement of a sharp dopant profile at the substrate/epi-layer interface. Less out-diffusion from the substrate would allow the use of thinner epitaxial layers, which would lead to a larger depletion width in the photoactive region. LPCVD also avoids, to a great extent, gas-phase nucleation, which would cause Ge particulates to fall onto the wafer surface during growth.
- (2) To reduce high levels of oxygen and copper present at the wafer interface, as observed by secondary ion mass spectroscopy (SIMS). In order to achieve high-quality epitaxial layers, it is imperative that the substrate surface be of excellent quality.

- (3) To make and test detectors, after satisfactory epitaxial layers have been made.

1.1. Extrinsic Germanium Photoconductors

In extrinsically-doped germanium, photoconductivity is observed when neutral impurities absorb incident infrared photons. The neutral impurities are ionized to produce free carriers. When the detector is biased, these free carriers will drift toward one of the contact electrodes, recombining with an ionized impurity atom after some distance, the average of which is known as the mean drift length. In a conventional detector (doped to about $10^{14}/\text{cm}^3$) operated at low temperatures (about 2°K), we find about $10^{14}/\text{cm}^3$ neutral acceptors. In high quality crystals, there are about $10^{11}/\text{cm}^3$ residual chemical donors (e.g., phosphorus), which are positively-charged (N_{D^+}), because they are compensated by the same concentration of negatively-charged compensating acceptors. The mean drift length is inversely proportional to the ionized acceptor concentration (N_{A^-}), because the free holes recombine with these acceptors. Since $N_{A^-} = N_{D^+}$, we find at low temperatures and low photon fluxes that the residual minority impurities dominate the mean free drift length, which in turn is proportional to the signal current.

1.2. Ge Blocked Impurity Band (BIB) Detectors

A BIB detector is a two-layer semiconductor, sandwiched between two heavily-doped contacts, one of which is optically-thin, in order to insure transmission of incident photons. The two-layer semiconductor structure is formed by growing an ultra-pure epitaxial layer on a heavily-doped substrate. The concentration of carriers in the substrate is high enough to cause limited impurity banding to occur. In Ge, this layer is doped to a concentration of about $10^{16}/\text{cm}^3$, as compared to $10^{14}/\text{cm}^3$ in conventional detectors (see Figs. 2 and 3). The impurity

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Fig. 2. Top: Schematic of a conventional detector; Bottom: schematic of a BIB detector; not drawn to scale (after [51]).

XBL 915-6719

Fig. 3. Top: Doping levels in a conventional detector: Bottom: doping levels in a Ge BIB detector (after [51]).

banding is a result of the overlap of the dopant atom wavefunctions, leading to extended wavelength response. The two-orders-of-magnitude increase in doping implies that the layer thickness can be decreased by two orders of magnitude without any loss in photon absorption. However, impurity banding also leads to conduction of charged carriers through the impurity band by the hopping mechanism [10,11]. This hopping of charged carriers from one ionized site to another produces undesirable dark currents in the device. ("Dark current" is current which flows through the device in the absence of photons, and is a source of noise in the detector). The pure epi-layer serves to suppress the hopping mechanism (hence the name "blocked impurity band"). When a reverse bias is applied across the device (see Fig. 4), the negative charges on the compensated acceptors are swept out of the heavily-doped layer, via hopping conduction through the impurity band. This results in a region depleted of ionized acceptors. Only neutral acceptors and positively-charged compensating donors remain in this depletion layer. Thus we see that the *minority* dopant concentration is the critical parameter in determining the "depletion region" in a BIB detector, in contrast to a depletion region in a P-N diode, which depends on the majority dopant concentration.

Since there are no negatively-charged ionized acceptors in the depletion region, a photo-generated hole cannot recombine with an ionized acceptor on its way through the pure blocking layer towards the contact electrode. Thus, there is one hole and one negative charge collected per ionization event across the depletion layer. This condition leads to a "gain of unity" for the detector. The fixed gain reduces generation-recombination noise that is present in conventional detectors, where the holes travel different distances before they recombine with an ionized acceptor. Only the holes which are excited into the valence band, produce photocurrents. Hopping conduction of the negative acceptor states is blocked by the pure layer. The depletion region is the photoactive region of the detector, since this is

Fig. 4. Schematics of space charge, electric field, and potential energy for a reverse-biased p-type BIB detector (after [51]). [XBL 884-1141]

where an electric field exists, and where photo-generated holes and ionized acceptor states can be collected; we would therefore want this region to be as wide as possible. The width of the depletion layer for a p-type detector, as given by Petroff and Stapelbroek [6], is

$$W = \left\{ \left[2\epsilon\epsilon_0(V_a - V_{bi})/(eN_D) \right] + t^2 \right\}^{1/2} - t, \quad (1)$$

where W is the width of the depletion layer, V_a is the applied voltage, V_{bi} is the built-in voltage of the junction between the pure epi-layer and the IR-active layer, ϵ is the dielectric constant of the semiconductor material, ϵ_0 is the permittivity of free space, e is the charge on an electron, N_D is the concentration of compensating donors, and t is the thickness of the pure epitaxial layer.

From eq. (1), we see that in order to increase the depletion width, we can either increase the applied voltage, decrease the minority impurity concentration, or decrease the epitaxial layer thickness. There is a limit to how much the applied voltage can be increased, since breakdown will occur at high enough voltages. Breakdown occurs at a much lower voltage in germanium than in silicon, due to the smaller binding energy of shallow impurities in Ge as compared to Si. Also, the larger Bohr radius of Ge ($\approx 80 \text{ \AA}$, as compared to $\approx 35 \text{ \AA}$ in Si), causes impurity banding to occur at concentrations of about $5 \times 10^{15} / \text{cm}^3$. This in turn leads to the requirement of a minority dopant concentration of about $10^{11} / \text{cm}^3$ to restrict hopping conduction and achieve depletion. Since single-crystal, ultra-pure germanium substrates are produced in our laboratory, it is assumed that the compensating donor concentration is low, although this has not been verified as of yet, since the lack of carrier freeze-out prevents us from obtaining this information with variable-temperature Hall effect. The only remaining viable parameter that can be altered in

order to increase the depletion width is to decrease the epitaxial layer thickness. This can only be realized if the concentration profile at the epi-substrate interface is very abrupt. In addition, in order for the epi layer to function as an effective blocking layer, it must have a low density of dislocations and interface states, which can act as deep traps. The pure epi layer must also be of the same type as the heavily-doped substrate (i.e., p-type epi on a p-type doped substrate, for example), in order to minimize the potential barrier at the interface.

2. EPITAXY

The word “epitaxy” comes from the Greek, and means “arranged upon”. Epitaxial growth therefore involves the growth of a single crystal film on top of a single crystal substrate. There are many ways in which the film material can be deposited on the substrate. Some of these methods include physical vapor deposition (PVD), liquid phase epitaxy (LPE), solid phase epitaxy (SPE), molecular beam epitaxy (MBE), vapor phase epitaxy (VPE), chemical vapor deposition (CVD), and low pressure chemical vapor deposition (LPCVD). Reviews of these techniques can be found in numerous papers and monographs [12-15]. Chemical vapor deposition is one of the more important and widely-used of these techniques. This is due to the fact that CVD allows for the deposition of a large number of elements and compounds at relatively low temperatures. A wide range of accurately-controllable stoichiometric compositions and layer structures are obtainable with CVD. Chemical vapor deposition will be discussed below, since it was the method employed in my work.

2.1. Chemical Vapor Deposition

In chemical vapor deposition, the reactant species, which typically is a molecule that contains the crystal growth species, must be transported to the substrate surface where, due to the high surface temperature, it can decompose to the desired species, which then laterally diffuses to a lattice site of the substrate. Growth of the epitaxial film then commences on the atomic steps of the crystal lattice. Alternatively, deposition can also occur by nucleation of particles in the gas phase. This, however, is highly undesirable, since it causes particulates to fall onto the wafer and create defects by impeding epitaxial growth.

2.1.1. Kinetics

Providing that the reaction under consideration is thermodynamically favorable, the kinetics of the reaction determine the growth conditions in chemical vapor deposition. The sequence of events is as follows:

- (1) diffusion of reactants to the substrate
- (2) adsorption of reactants at the surface
- (3) surface events such as chemical reaction, surface motion, lattice incorporation, etc.
- (4) desorption of products from the surface
- (5) diffusion of products away from the surface.

The slowest of the above steps will be the one that is the “rate-determining step” for the overall process.

The growth rate of a CVD process will vary with temperature, as indicated in Fig. 5. Although the growth rate is an increasing function of temperature for all values of T , there are two distinct temperature regimes, demarcated by a transition temperature T^* . For temperatures above T^* , the growth rate is high, and increases very slowly with temperature, whereas the growth rate is highly temperature

Fig. 5. Typical growth-rate curve of a chemical vapor deposition process.

dependent for temperatures below T^* . The low temperature ($T < T^*$) regime is characterized by high activation energy, and the growth is controlled by the slow surface reaction rate. The activation energy can therefore be thought of as a measure of the “difficulty” of achieving a certain reaction, and will be determined by the rate-controlling step. In general, the growth rate is governed by an Arrhenius-type equation:

$$G = G_0 \exp[-\Delta E/kT_s] , \quad (2)$$

where G is the reaction rate, ΔE is the activation energy, k is Boltzmann’s constant, and T_s is the temperature of the substrate.

If the surface reaction rate was the main limiting factor, the growth rate above the transition temperature would be represented by the dotted line in Fig. 4. At high temperatures, however, growth becomes limited by the rate at which the gaseous compound can diffuse through the fluid boundary layer above the growing film. This rate of diffusion through the boundary layer becomes much less than the rate at which the gaseous compound is decomposed at the interface. This latter rate increases exponentially with T , while the diffusion coefficient of the gas through the boundary layer increases relatively slowly with T (roughly proportional to $T^{1.5-2.0}$). Hence, at sufficiently high temperatures, the overall growth process will become limited by the rate of the diffusion step. Most epi-reactors are in fact operated in this diffusion-limited regime, so that the growth rate is relatively insensitive to factors such as variations of the substrate orientation.

2.2. Low Pressure Chemical Vapor Deposition

The epitaxial layers grown by Rossington at atmospheric pressure using GeH_4 [9] suffered from defects that were caused by gas phase nucleation of Ge particles falling onto the surface. In addition, there was an unacceptable variation in growth rate across the wafer. Thirdly, there was significant out-diffusion of Ga from the substrate, causing a diffusion tail of approximately $5-8\text{ }\mu\text{m}$. A review of the literature [15-20] shows that operating in the low pressure range greatly reduces these problems. Films produced at low pressures exhibit better uniformity, have fewer pinholes, and, for Si, can be grown at temperatures that are about $100-200^\circ\text{C}$ lower than for atmospheric pressure systems [see 18]. Also, the boundary-layer width increases at reduced pressures (for the same gas velocity), causing a significant reduction in both auto-doping effects and gas-phase nucleation. In addition, no carrier gases are needed with low pressure deposition, thus reducing hydrogen absorption on the surface of the wafer [20]. LPCVD systems do have some drawbacks associated with them, however. For example, the thermal resistance between the wafer and the susceptor increases at low pressures, resulting in a $100-150^\circ\text{C}$ difference in their mean temperatures. LPCVD systems are also more difficult to maintain, because the pump and pressure gauges may be subjected to highly corrosive atmospheres.

2.3. Germanium Epitaxy

2.3.1. Epitaxy using GeH_4

The first experiments that I ran extended the work of Rossington [9] by using GeH_4 as the source gas, but running the deposition at low pressure. The pyrolysis of GeH_4 is similar to that of SiH_4 , which is commonly used in silicon epitaxy. The pyrolysis is a thermal decomposition of the GeH_4 on the hot susceptor surface. The reaction is expressed as

This reaction has the advantage of not being reversible, and having no corrosive by-products. The germane process has two inherent problems, however. One is that since homogeneous nucleation is possible, gas phase nucleation is hard to suppress completely. This can be controlled in the low pressure process. The germane process is also very sensitive to the presence of oxidizing species, which can lead to the formation of particulates, and thus poor layer quality.

There is very little literature on chemical vapor deposition of Ge on Ge substrates. Early work was hampered by the difficulty of obtaining GeH_4 of sufficient purity. High quality epitaxial layers were prepared by Roth et al. [21]. Among the first to report homoepitaxial growth were Davis and Lever [22], who needed to heat their substrates to 900°C . Christensen [23] was able to obtain homoepitaxial growth at 550°C . This lower epitaxial temperature was thought to be related to a higher purity of germane and a better substrate surface. Tamaru et al. [24,25] examined the kinetics of germane pyrolysis, and concluded that the decomposition proceeds about one order of magnitude faster on the substrate surface than in the gas phase. They postulated that the GeH_x radicals migrate freely on the germanium surface, and thus promote high crystalline perfection. Some other work has been done on chemical vapor deposition of Ge on other substrates, such as GaAs [26,27], and Si [28-30]. Much work has been done on epitaxial growth using silane SiH_4 on silicon [31-46], and many of these results can be extended to the growth of germanium epitaxial layers.

There has been renewed interest recently in germanium epitaxy, which has been generated by work on strained-layer epitaxy. In order to maintain a high degree of crystalline perfection at the interface between two different materials, the lattice constants of the two materials should be matched as closely as possible. In

the case of Ge and Si, there is a 4.2% difference in their lattice constants, which leads to the generation of one misfit dislocation every twenty-five silicon atoms [47]. These dislocations can act as traps and recombination centers. Epitaxial layers that are sufficiently thin can deform elastically to match the lattice spacing of the substrate, thus reducing interfacial dislocations (see Fig. 6). This deformation lowers the surface energy associated with the dangling bonds, while increasing the stored strain energy within the epitaxial layer. At some epitaxial layer thickness, the strain energy exceeds the surface energy, causing the material to revert back to its unstrained structure [48]. This critical thickness is plotted in Fig. 6 for a $\text{Ge}_x\text{Si}_{1-x}$ strained layer on a Si substrate. It is seen that the critical thicknesses are much larger than those predicted by equilibrium theory, and are in a range that is useful for device applications [48]. Modulation doping of GeSi/Si has been used successfully to make heterojunction transistors [49]. Multiple, regularly-repeated GeSi/Si strained layers lead to strained layer superlattices whose artificially-induced periodicities greatly alter the basic physical properties of the material. Moriarty and Krishnamurthy [50] predict that GeSi/Si superlattices might exhibit enhanced carrier mobilities, and may lead to the creation of a “direct bandgap” semiconductor through “zone-folding” in the Brillouin zone.

2.3.1.1. Apparatus

A schematic of the horizontal CVD apparatus used to deposit the undoped Ge epitaxial layers on the IR-active substrate is shown in Fig. 7 [51]. The Ge substrates sit on a silicon carbide-coated graphite susceptor, which is inductively heated by an external RF source. Pure, undiluted GeH_4 is used as the Ge source. Figs. 8 and 9 show photographs of the horizontal epitaxial reactor. The mechanical pump was modified at the beginning of these tests to increase the pumping speed by installing a larger diameter tube. A liquid nitrogen cold trap was also added to condense the GeH_4 gas, preventing it from running through the pump and causing

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Fig. 6. Accommodation of strain in epitaxial growth. The curve shows the experimentally-determined limits for defect-free strained-layer epitaxy of $\text{Ge}_x\text{Si}_{1-x}$ on Si. The insets show the atomic arrangements for the strained but defect-free material found in sufficiently thin layers, and for the bulk material in which misfit dislocations accommodate the lattice mismatch. The diagrams greatly exaggerate the degree of lattice mismatch, which is about 4.2% for pure Ge on Si [48].

Fig. 7. Schematic of horizontal CVD epi reactor (after [51]). [XBL 884-1189]

Fig. 8. Photograph of epitaxial reactor, with view of extension tube. [CBB 913-2118]

Fig. 9. Close-up photograph of quartz tube, showing heated graphite susceptor and germanium substrate. [CBB 902-1342]

corrosion. Adsorbed GeH_4 was then flushed out with warm nitrogen gas, and vented.

2.3.1.2. Substrate choice and preparation

A number of crystals were used in the development of germanium epitaxial layers. Both (100) and (113) crystal orientations were studied. N-type germanium wafers, with a residual dopant concentration of about $10^{11}/\text{cm}^3$, were used for the electrical characterization of the epitaxial layers, which are typically p-type due to residual copper contamination. This choice will provide junction isolation. The p-type substrates (doped to a level of about $2 \times 10^{16}/\text{cm}^3$, with low compensation) are used for germanium BIB detectors.

In order to achieve high quality epitaxial layers, the substrate surface must be of excellent quality. Various cleaning techniques were investigated to reduce the oxygen and carbon content at the substrate/epi-layer interface. The interface quality was monitored by Secondary Ion Mass Spectroscopy (SIMS) analysis.

Following the approach taken by Gregory et al. [52], oxide films are grown on the surface of the germanium wafer using $\text{H}_2\text{O}_2/\text{HF}$ solutions, following a treatment of boiling TCA, boiling acetone, boiling methanol, and boiling distilled water. The purpose of this procedure is to consume the top layer of the Ge wafer. The oxide is then etched away with a (20:1) HNO_3/HF solution, leaving behind a virgin surface. Several variations of this cleaning method were tried. Several attempts were also made to remove the remaining surface oxide *in situ*, including a high-temperature hydrogen plasma bake, a high-temperature helium plasma bake, a high-temperature hydrogen bake without plasma, and a high-temperature bake to desorb the surface oxide. Fig. 10 shows SIMS data on oxygen for three epitaxial growth runs. All three runs show an oxygen concentration above the SIMS machine background. Excessively high concentrations were found when the reactor

Fig. 10. SIMS data showing oxygen profiles for three epitaxial growth runs. Samples #1 and 2 received a clean with plasma etch. Sample #4 was grown when there was a leak in the reactor. Profiles labeled "repeat" are spurious data. [XBL 914-762]

had a leak. Fig. 11 shows the carbon concentration measured by SIMS for the same layers shown in Fig. 10. The *in situ* plasma etching process clearly introduced carbon, and so this step was eliminated. Several tests were also run to judge the effect of a final methanol rinse on the carbon content in the film. Figs. 12-14 show SIMS data from runs 16, 17 and 19. Sample #1 (run 17) was run at 550°C, and a flowrate of 10 standard cubic centimeters per minute (sccm), with an H₂O₂ clean using a methanol rinse and a hydrogen bake. Sample #2 (run 16) was run at 550°C and 10 sccm, with a 7:2:1 (HNO₃:HF:Fuming HNO₃) clean, using no methanol or H₂. Sample #3 (run 19) was grown at 550°C, 10 sccm, with an H₂O₂ clean, with no methanol, but with H₂. The SIMS data show high carbon and oxygen concentrations at the epi interface, and throughout the film. The high surface concentrations are probably due to surface particulate material. Average oxygen concentrations for the epi-layers are 2.3×10^{18} , 3.8×10^{18} , and 4.8×10^{18} atoms/cc, and average carbon concentrations for the epi-layers are 1.7×10^{19} , 2.1×10^{19} , and 3.0×10^{19} atoms/cc for samples 1, 2, and 3, respectively, ignoring high surface concentration peaks.

2.3.1.3. Epitaxy procedure

A matrix of tests were run in which the temperature was varied from 400°C to 650°C, and the GeH₄ flowrate was varied from 1-20 sccm (see Table 1).

2.3.1.4. Characterization of the epitaxial layers

The structural quality of the epitaxial layers was assessed visually with the optical microscope, and with Rutherford backscattering. The thicknesses of the epitaxial layers were determined by weighing the wafers before and after deposition, and assuming that the density of the layers was equal to that of bulk germanium (the actual film density is dependent on the deposition parameters [53]). The highest quality Ge epitaxial layers were grown on Ge substrates under the following

Fig. 11. SIMS data showing carbon profiles for three epitaxial growth runs. Samples #1 and 2 received a clean with plasma etch. Sample #4 was grown when there was a leak in the reactor. Profile labeled "repeat" is spurious data. [XBL 914-761]

Fig. 12. SIMS data showing oxygen and carbon profiles for run #17. [XBL 914-760]

Fig. 13. SIMS data showing oxygen and carbon profiles for run #16. [XBL 914-759]

Fig. 14. SIMS data showing oxygen and carbon profiles for run #19. [XBL 914-758]

Table 1. Growth runs using GeH_4

Crystal No.	Substrate conc. (cm^{-3})	Pre-deposition	Growth temp.	GeH_4 flow rate	Pressure	Film type	Film thickness	Surface appearance
1) Eagle-Picher	Ge:Ga (113) [Ga] = 1×10^{16}	650°C bake	660°C	20 sccm	40 mTorr		6 μm	blotchy
2) 734	Ge:P (113) [P] = 2×10^{14}	He plasma	620°C	20 sccm	40 mTorr		7 μm	pitted
3) 736	Ge:P (100) [P] = 1×10^{14}	H_2 plasma 580°C	580°C	5 sccm	10 mTorr		51 μm	polycrystalline
4) 734	Ge:P (113) [P] = 2×10^{14}	H_2 plasma 650°C	580°C	5 sccm	10 mTorr		~3 μm	sample etched
5) 729	Ge:P (113) [P] = 6×10^{13}	H_2 plasma 550°C	475°C	5 sccm	10 mTorr		2 μm	streaky
6) 729	Ge:P (113) [P] = 6×10^{13}	640°C bake no hydrogen	640°C	5 sccm	10 mTorr	slightly p-type	sample etched	etch pits
7) 636	Ge:P (113) [P] = 5×10^{11}	650°C bake no hydrogen	650°C	10 sccm	23 mTorr	strongly p-type	12 μm	small polycrystalline grains
8) 636	Ge:P (113) [P] = 5×10^{11}	650°C bake no hydrogen	600°C	10 sccm	22 mTorr	strongly p-type	6 μm	tiny polycrystalline grains; smooth
9) 636	Ge:P (113) [P] = 5×10^{11}	650°C bake no hydrogen	550°C	10 sccm	22 mTorr	strongly p-type	8 μm	shiny, very smooth
10) 636	Ge:P (113) [P] = 5×10^{11}	650°C bake	500°C	10 sccm	22 mTorr	p-type	7 μm	shiny

Table 1. (continued) Growth runs using GeH_4

Crystal No.	Substrate conc. (cm^{-3})	Pre-deposition	Growth temp.	GeH_4 flow rate	Pressure	Film type	Film thickness	Surface appearance
11) 636	Ge:P (113) [P] = 5×10^{11}	650°C bake	450°C	10 sccm	22 mTorr	strongly p-type	14 μm	shiny
12) 636	Ge:P (113) [P] = 5×10^{11}	650°C bake	400°C	10 sccm	21 mTorr	strongly p-type	sample etched	tiny hillocks
13) 636	Ge:P (113) [P] = 5×10^{11}	640°C bake	400°C	10 sccm	22 mTorr	strongly p-type	no growth	
14) 636	Ge:P (113) [P] = 5×10^{11}	650°C bake	400°C	2 sccm	1.5 mTorr	strongly p-type	0.2 μm	streaky, many pinholes
15) 636	Ge:P (113) [P] = 5×10^{11}	645°C bake	400°C	5 sccm	9.5 mTorr	strongly p-type	0.6 μm	white patches
16) 636	Ge:P (113) [P] = 5×10^{11}	640°C bake 7:2:1 clean	550°C	5 sccm	9.5 mTorr	strongly p-type	1.1 μm	cloudy
17) 636	Ge:P (113) [P] = 5×10^{11}	635°C bake w/ MeOH rinse	550°C	10 sccm	21 mTorr	p-type	1 μm	very cloudy
18) 636	Ge:P (113) [P] = 5×10^{11}	700°C w/o MeOH rinse	550°C	10 sccm	21 mTorr	strongly p-type	1.75 μm	shiny, slight haze
19) 636	Ge:P (113) [P] = 5×10^{11}	H ₂ bake, 700°C no MeOH	550°C	10 sccm	21 mTorr		1.84 μm	shiny, slight haze
20) 736	Ge:P (100) [P] = 1×10^{14}	740°C bake	550°C	10 sccm	21 mTorr		13 μm	highly pitted

conditions:

1. Pure GeH_4 ; flowrate = 10 sccm; pressure ≈ 20 mTorr.
2. Substrate temperature = 550°C .
3. Ge growth rate = $0.5\ \mu\text{m/hr}$.
4. Pre-deposition bake at 650°C to desorb the native oxide.

Fig. 15 shows optical micrographs that demonstrate the effect of the H_2 plasma reducing step on the quality of the epitaxial layers on (100) and (113) substrates. The (100) sample, treated with a hydrogen plasma, led to a polycrystalline layer (Fig. 15a). The (113) sample, treated with a hydrogen plasma, etched (Fig. 15b). The (113) sample grown at 550°C without hydrogen plasma led to a single crystal deposition (Fig. 15c). This further corroborated the need to remove the plasma treatment from the pre-deposition process.

Figs. 16-20 show Rutherford backscattering (RBS) data for Ge epi layers grown on crystal substrate #636, at substrate temperature intervals of 50°C from 400°C to 650°C . All of the epi layers appear to be single crystal, except for a "cloudy region" on the 550°C sample. This region has a higher (RBS) yield than the substrate, indicating a high concentration of defects. In all of the samples, the dechannelling of the substrate is higher than in the epi-layer. This is probably due to damage of the substrate by etching, or by beam damage during alignment of the sample.

Fig. 21 shows scanning electron micrographs (SEMs) of runs 19 and 20. These runs were carried out after the addition of a glass-to-metal seal at the entrance to the quartz chamber, and the addition of silicone O-rings to replace the viton O-rings. Although these system modifications were intended to decrease carbon and oxygen contamination in the films, both of the films produced were of poor quality. The surface of run #19 (Fig. 21a) on a (113) substrate was covered with

(a)

0.03 mm

(b)

0.03 mm

(c)

0.03 mm

Fig. 15. Optical micrographs of GeH_4 epilayers: (a) run #3; (b) run #4; (c) run #9.
[XBB 914-2750]

Fig. 16. RBS data for epitaxial film growth on crystal substrate #636 at 400°C.

[XBL 914-757]

Fig. 17. RBS data for epitaxial film growth on crystal substrate #636 at 450°C.

[XBL 914-756]

Fig. 18. RBS data for epitaxial film growth on crystal substrate #636 at 550°C.

[XBL 914-755]

Fig. 19. RBS data for epitaxial film growth on crystal substrate #636 at 600°C.

[XBL 914-754]

Fig. 20. RBS data for epitaxial film growth on crystal substrate #636 at 650°C.

[XBL 914-753]

(a)

0.5 μm

(b)

3.3 μm

Fig. 21. Top: Scanning electron micrograph (SEM) of run #19 on a (113) substrate; growth rate is $0.61 \mu\text{m/hr}$. Bottom: SEM of run #20 on a (100) substrate; growth rate is $4.3 \mu\text{m/hr}$. [XBB 914-2748]

small dimples, and the surface of run #20 (Fig. 21b), on a (100) substrate, was highly pitted. The growth rate on the (100) substrate was seven times faster than on the (113) substrate (4.3 $\mu\text{m/hr}$ vs. 0.61 $\mu\text{m/hr}$). All of the epi-layers measured were p-type, as determined by the thermal probe method.

Hall effect measurements were used to examine the net dopant concentration and compensation level. Fig. 22 shows the freeze-out curve of a Ge epi-layer grown on an n-type (113) substrate. The residual acceptor concentration was $\approx 10^{14}/\text{cm}^3$. The acceptor ionization energy, as determined from the slope of the low-temperature portion of the curve, is 44 meV, which identifies the acceptor as copper. Copper, being a deep triple acceptor [54], is not thought to significantly influence the BIB detector operation. As was discussed in section 1.2, the depletion width in a BIB detector is determined by the compensating donor concentration. Therefore, the presence of copper should not be a first-order effect.

2.3.1.5. Summary of epitaxy using GeH_4

An LPCVD technique for the low-temperature growth of epitaxial Ge layers was developed. Hall effect data showed the layers to be p-type, due to residual copper contamination. SIMS data revealed that the oxygen and carbon concentrations at the epi-layer/substrate interface need to be reduced further.

At this point in the course of my experiments, the laboratory was relocated to the new Advanced Materials Laboratory (AML) building at the Lawrence Berkeley Laboratory. This necessitated moving the epi-rig, and re-installing it. In addition, new safety requirements specified that GeH_4 could not be used in the new building. Operation of the system had to be carried out with tetramethylgermanium, a relatively untried liquid source. Installation of the epi-rig in the new building took six months to complete, during which time the opportunity was taken to make major modifications to the system, mainly for the purposes of improving the cleanliness of

Fig. 22. Variable-temperature Hall effect measurements of a Ge epilayer on an n-type (113) substrate. The hole freeze-out curves indicate a light copper contamination. The two curves (+,*) are measurements of the same sample, and demonstrate reproducibility (after [51]). [XBL 914-752]

the operation. These modifications will be discussed below.

2.3.2. System Modification after Relocation of Apparatus

The primary improvement made to the system was the installation of a longer loading tube. This allows the samples to be loaded directly from the final cleaning area into the chamber, remaining at all times under laminar flow. A removable glass sheath is used to transport the quartz sled, containing the sample, into the chamber. The glass sheath must make very precise contact with the quartz reaction tube, so that the sled can move smoothly into the quartz tube. A new end-plate was also designed and installed, with two O-rings, allowing differential pumping there, also. The entire hood housing the epitaxial growth rig was lined with stainless steel, and now contains no flammable parts. All relevant schematic diagrams of the apparatus are included in Appendix III.

2.3.3. Epitaxy using $\text{Ge}(\text{CH}_3)_4$

Tetramethylgermanium ($\text{Ge}(\text{CH}_3)_4$) is a volatile, flammable liquid. It has mostly been used as an n-type dopant for gallium arsenide and other III-V semiconductors. It can also be used to deposit germanium by organometallic vapor phase epitaxy (OMVPE). Kahn et al. [55] deposited epitaxial layers by the pyrolysis of $\text{Ge}(\text{CH}_3)_4$ on (111) germanium substrates at 550–650°C. Avigal et al. [56] also studied the pyrolysis of tetramethylgermanium and tetraethylgermanium, and found that good quality films could be obtained if the substrates received an *in situ* HCl etch, growth occurred in the presence of H_2 , and deposition temperatures exceeded 850°C. They found the level of carbon contamination on the Ge substrates to be 25 ppm. Venkatasubramanian et al. [57] found the growth rate to be negligible in the temperature range 675–825°C, with the use of TMGe as the Ge source.

2.3.3.1. Apparatus

Since the vapor pressure of TMGe is high (139 Torr at 0°C), it was decided not to bubble the liquid, but rather to run the vapor (which sits on top of, and is in equilibrium with, the liquid) as the gas source. To do this, the inlet to the bubbler was capped off, and the outlet was run directly through the mass flow controller (MFC) into the chamber. (Note that the MFC requires a pressure drop of about 250 Torr across it in order to function properly. In order for the pressure to be sufficient, and for ease of operation, the bubbler was maintained at room temperature, which corresponds to a vapor pressure of about 400 Torr). Also, since it was forbidden to run with hydrogen in the new building, helium was used as a carrier gas (see Fig. 23).

2.3.3.2. Epitaxy procedure

My initial attempts to grow epitaxial layers were based on the following considerations:

1. The maximum inlet flow rate to the chamber is 35 sccm, but the molecular drag pump works most efficiently in the 10–20 sccm range. This corresponds to a pressure range of approximately 15–40 mTorr (read from the N₂ curve in Fig. 24). The pumping speed for hydrogen drops off drastically above about 75 mTorr of inlet pressure (see Fig. 25).
2. Based on the results of Avigal et al [56], the optimum mole fraction of TMGe to He is about 1%. Running the hydrogen flow at 10–20 sccm would require the TMGe to be run at 0.1–0.2 sccm. The only available low-flow MFC allowed a maximum flow of 20 sccm, and was calibrated for GeH₄. The MFC can only control the flow reliably down to a flow rate of about 1 sccm.

Consequently, the following deposition parameters were chosen to be varied:

Pressure in chamber: 10–40 mTorr.

XBL 913-4777

Fig. 23. Gas manifold for epitaxial runs using $\text{Ge}(\text{CH}_3)_4$ as the germanium precursor.

Fig. 24. Inlet flow vs. chamber pressure for the Alcatel Molecular Drag Pump 5010. [XBL 914-751]

Fig. 25. Pump speed vs. inlet pressure for the Alcatel Molecular Drag Pump 5010.
[XBL 914-750]

TMGe mole fraction: 5–20% (1–4 sccm).

Deposition temperature: 600–750 °C.

The growth attempts are described in Table 2.

2.3.3.3. Discussion of epi growth attempt using $\text{Ge}(\text{CH}_3)_4$

Several problems were encountered while attempting to grow epi layers using $\text{Ge}(\text{CH}_3)_4$. One of the first difficulties encountered was an initial inability to accurately control the pressure. In addition, the TMGe flow took several minutes to drop to zero after closure of the valve. This suggested that the TMGe was condensing in the lines, and/or in the MFC. To remedy this, heat tape was wrapped around all of the stainless steel lines, and the MFC, and the Variac controller was set to control the temperature of the heat tape at 30–35 °C. This is above room temperature, but below the maximum tolerable temperature for the MFC, which is 45 °C. The heat tape was installed just prior to run #8, and seemed to completely alleviate the condensation problem. Pressure and flow were thereafter controllable.

Runs #1-9 were carried out using either He as a carrier gas, or with straight TMGe vapor. Aside from two anomalous results that could not be repeated (runs #5 and 10), no growth of epi layers could be achieved. Based on results reported in the literature [55,56], it was decided that hydrogen should be used as the carrier gas. Observing proper safety procedures, runs #10-17 were carried out using H_2 as the carrier gas.

Limited by the available mass flow controllers at hand, only certain gas flow ratios could be used to attempt to achieve the desired mole fraction of TMGe. The difficulty was compounded by the necessity of running the TMGe vapor through an MFC that was calibrated for GeH_4 . It seems reasonable to expect that the flow rate of $\text{Ge}(\text{CH}_3)_4$ would be different than that of GeH_4 , since their molecular weights are vastly different [see 58,59]. Unfortunately, the calibration factor for TMGe was

Table 2. Growth runs using $\text{Ge}(\text{CH}_3)_4$

Crystal No.	Substrate conc. (cm^{-3})	Mole fraction of TMGe	Growth temp.	Carrier gas	Pressure	Film type	Film thickness	Surface appearance
1) 740	Ge:P (100) [P] = 9×10^{13}	100%	600°C	None	20 mTorr	slightly n-type	-0.3 μm (etched)	hazy and streaky
2) 740	Ge:P (100) [P] = 9×10^{13}	19%	600°C	He	19 mTorr	neutral	no growth	shiny
3) 740	Ge:P (100) [P] = 9×10^{13}	50%	590°C	He	30 mTorr	neutral	no growth	shiny
4) 740	Ge:P (100) [P] = 9×10^{13}	50%	710°C	He	30 mTorr	slightly n-type	no growth	severely pitted
5) 740	Ge:P (100) [P] = 9×10^{13}	100%	760°C	none	16 mTorr	slightly n-type	16 μm	many stacking faults
6) 740	Ge:P (100) [P] = 9×10^{13}	100%	770°C	none	22 mTorr		no growth	pitted
7) 740	Ge:P (100) [P] = 9×10^{13}	100%	750°C	none	19 mTorr		no growth	pitted
8) 702	Ge:P (111) [P] = $1-2 \times 10^{11}$	100%	780°C	none	20 mTorr		no growth	pitted
9) 702	Ge:P (111) [P] = $1-2 \times 10^{11}$	100%	780°C	none	20 mTorr		no growth	pitted
10) 736	Ge:P (100) [P] = 1.8×10^{14}	1.7%	800°C	H ₂	14 Torr	p-type	3 μm	many small hillocks

Table 2. (continued) Growth runs using $\text{Ge}(\text{CH}_3)_4$

Crystal No.	Substrate conc. (cm^{-3})	Mole fraction of TMGe	Growth temp.	Carrier gas	Pressure	Film type	Film thickness	Surface appearance
11) 736	Ge:P (100) [P] = 1.8×10^{14}	1.7%	800°C	H ₂	2 Torr	(plasma)		covered w/black hydrocarbons
12) 736	Ge:P (100) [P] = 1.8×10^{14}	1.7%	550°C	H ₂	14 Torr	slightly p-type	no growth	shiny, small pits
13) 736	Ge:P (100) [P] = 1.8×10^{14}	1.7%	630°C	H ₂	14 Torr		no growth	shiny
14) 736	Ge:P (100) [P] = 1.8×10^{14}	1.7%	725°C	H ₂	14 Torr		no growth	black soot
15) 736	Ge:P (100) [P] = 1.8×10^{14}	1.7%	800°C	H ₂	14 Torr		no growth	black soot
16) 736	Ge:P (100) [P] = 1.8×10^{14}	3.0%	850°C	H ₂				sample melted
17) 736	Ge:P (100) [P] = 1.8×10^{14}	3.0%	700°C		atmospheric		no growth	vapor pressure of TMGe < atm.!

unknown (Russ Aber, Tylan General, personal communication). Using a technique discussed in Appendix I, it was ascertained that the flowrate of TMGe through the GeH_4 mass flow controller was 69% lower than it would have been for GeH_4 , at the same setting. This implies that the actual flowrate at a setting of 20 sccm was actually only about 6 sccm. This further constrained my ability to obtain the desired mole fraction of about 1%.

In the first growth attempt using hydrogen as the carrier gas (run #10), 3.4 sccm of TMGe was run with 200 sccm of H_2 , for a 1.7% mole fraction ratio. This resulted in a pressure of about 14 Torr in the chamber. Since the pumping speed of hydrogen is essentially zero at this pressure, the flow rates were halved for the next run (#11), while maintaining the same mole fraction. This led to a pressure of about 2 Torr, at which the pumping speed was still essentially zero. Since the MFC cannot reliably control flowrates below 1 sccm, this was the lower limit of operation. At this growth temperature of 800°C , corresponding to an RF power of 4.0 kV, the hydrogen gas struck a plasma, covering the quartz chamber and graphite susceptor with black hydrocarbon soot.

I then proceeded to check the plasma range of H_2 at various kV settings. At 4.0 kV (800°C), a hydrogen plasma exists between 70 mTorr to 3.4 Torr. For kV settings below 3.25, corresponding to 720°C , no plasma exists, over the entire range of pressures (up to atmospheric). Hence, in order to run at higher temperatures, the system would have to be run at pressures above 3.4 Torr, despite the fact that the pumping speed was very low at those pressures. The system could not be run at pressures below 70 mTorr, due to the need to have the proper mole fraction, and the limitations of the MFC.

The high growth temperatures, although undesirable from the BIB detector point of view, were tried, since it seemed that the TMGe was not cracking, since there was no discernable epi growth. As mentioned by Venkatasubramanian et al.

[57], the TMGe may have been only partially cracking (as evidenced by the black hydrocarbon deposits), leaving behind a germanium-bearing species that was also volatile.

A few lower temperature runs (#12-14) were also attempted, and they too resulted in no epi growth. Thought was given to running the TMGe at atmospheric pressure, but that would require bubbling, as the vapor pressure of TMGe is less than atmospheric.

After reading reference [57], I contacted the group at the Research Triangle Institute. They claimed to have *never* obtained successful epitaxial growth using TMGe. They did run GeH₄ in their lab, and claimed to achieve sharp interfaces. Substrate samples were sent to them to perform some tests using GeH₄, while at the same time I began to look into the possibility of using germanium tetrachloride GeCl₄, another liquid source.

2.3.4. Epitaxy using Germanium Tetrachloride GeCl₄

Growth of germanium epitaxial layers from GeCl₄, which has been the most extensively used technique for the growth of Ge epi-layers, occurs through a reduction reaction that uses hydrogen as the reducing agent. The following reaction takes place on the hot substrate:

The HCl formed may, in turn, react with the solid Ge to form other gaseous species detected in the GeCl₄–H₂ system [60], such as GeCl₂ and GeCl₃. The situation in the reactor is considerably more complex than that suggested by the overall reaction given above. Three points should be noted about the above reaction:

1. The hydrogen is both a carrier and an active participant in the reaction;
2. Gaseous HCl is formed;
3. The reactions are reversible.

The earliest work on the reduction of GeCl_4 with hydrogen for epitaxial deposition was reported by Sheftal et al. [61]. They studied deposition of homoepitaxial germanium at 850°C . Matovich and Andres [62] achieved epitaxial growth at temperatures as low as 575°C . Cave and Czorny [63] investigated the preparation of doped epitaxial germanium layers on (111) germanium substrates by GeCl_4 reduction. They obtained growth rates of $0.1\text{--}8.0\text{ }\mu\text{m}/\text{min}$ at temperatures ranging from $600\text{--}920^\circ\text{C}$. Gavrilov et al. [64] studied phosphorus doping of Ge epitaxial films obtained by co-reduction of GeCl_4 and PCl_3 with hydrogen, and found that the deposition rate of the doped films was less than for undoped films, as a result of secondary etching reactions on the surface. In addition, the doping concentration was found to depend only on the PCl_3 concentration, and was independent of the concentration of GeCl_4 . The dislocation density in the films was controlled by the ratio of PCl_3 and GeCl_4 concentrations in the initial gas mixture.

Miller and Grieco [65] studied the etching reactions involving Ge-HCl and Ge-GeCl_4 . Grossman [66] has described a kinetic theory for the origin of auto-doping for the epitaxial process. Other investigators [67-72] examined growth conditions and surface morphology for different crystallographic orientations. Silvestri [60] observed that at deposition temperatures from $600\text{--}850^\circ\text{C}$, the deposition rate was essentially independent of either the temperature or of the hydrogen flow rate, but varied linearly with the GeCl_4 flux. He concluded from this that the deposition rate was controlled by mass transfer. At temperatures below 600°C , on the other hand, the deposition reaction was not complete. More recent work by Ishii and Takahashi [73] studied the etching and growth of germanium films in the

temperature range 490–565°C. At relatively low partial pressures of the GeCl_4 (less than about 2×10^{-3} Torr) epitaxial growth of Ge was observed on Ge (100) surfaces, whereas at higher partial pressures, etching of the Ge occurred. They found that at 540°C, and at GeCl_4 partial pressures of 1.3×10^{-2} Torr, the etching rate of germanium is independent of the partial pressure of the hydrogen, between 0 and 7.5 Torr. The etching rate follows a reverse disproportionation reaction: $\text{Ge(s)} + \text{GeCl}_4\text{(g)} \rightarrow 2\text{GeCl}_2\text{(g)}$. In addition, they claim that growth does not occur through the gas-phase reduction of GeCl_4 by hydrogen, but rather through a surface reaction between two hydrogen atoms dissociatively adsorbed and a surface-adsorbed GeCl_2 molecule. They required hydrogen partial pressures 2000–7000 times greater than that of the GeCl_4 in order for epitaxial growth to occur. Growth attempts in the presence of He instead of H_2 resulted in no Ge film growth, and only etching occurred.

Since Rockwell was successfully growing epilayers for BIB detectors using GeCl_4 [5], duplication of their process as closely as possible was attempted.

2.3.4.1. Apparatus

Since the vapor pressure of GeCl_4 is 76 Torr at 20°C, it would not be possible to run direct vaporization with GeCl_4 , as was done with the TMGe. It therefore became necessary to bubble H_2 gas through the liquid. In order to allow this, the gas lines were re-configured, as shown in Fig. 26. As shown in the figure, the output from the hydrogen purifier was initially divided into two flows: one sent to the bubbler, and one to be used downstream as a carrier gas.

2.3.4.2. Epitaxy procedure

The epitaxy system at Rockwell International is run with a hydrogen flowrate of 20 l/min, a velocity of 10–20 cm/sec at atmospheric pressure [Jim Huffmann, personal communication]. Their system is also run at a $\text{GeCl}_4\text{:H}_2$ mole fraction of

XBL 913-4778

Fig. 26. Gas manifold for epitaxial runs using GeCl_4 as the germanium precursor. Bubbling is carried out with H_2 , which is also used as the carrier gas downstream.

10^{-3} , and a deposition temperature of 736–765 °C. Given the capacity of our H_2 mass flow controller, the maximum flowrate obtainable in our chamber would be about 8 cm/sec. The hydrogen velocity is further reduced when the flow is limited by the maximum output of the hydrogen purifier, which is 5 standard liters per minute (slm), resulting in a velocity of about 4 cm/sec. To achieve a $GeCl_4:H_2$ ratio of 10^{-3} , it was necessary to run the 10 slm mass flow controller at 100% of capacity, and the 1000 sccm H_2 mass flow controller at 13% of capacity. The relevant calculations are outlined in Appendix II.

It was therefore decided to attempt to grow epitaxial films by varying the Ge mole fraction from 10^{-3} to 10^{-4} , and varying the deposition temperature from 650–800 °C. It was initially intended that growth be attempted at low pressures, but this became impossible for reasons that are discussed below, and all growth attempts were run at atmospheric pressure.

One condition that is imperative in order to achieve acceptable epitaxial growth is having a surface that is free of oxide or other forms of damage. Surface damage that is caused by the slicing of the ingot is removed by mechanical lapping and chemical polishing. Typically, the wafer is subjected to a high-temperature HCl etch, to remove the native oxide, and cause the surface carbon to diffuse into the bulk. Rockwell performed an *in situ* HCl etch at 820 °C to remove about 0.5 μm of the surface before beginning growth. Our system was not capable of pumping HCl, due to its highly corrosive nature.

My first tests explore the effects of a high-temperature hydrogen bake to reduce the native oxide on the wafer surface. In my first attempts, the inlet to the bubbler was open and the outlet was closed. This resulted in $GeCl_4$ vapors backing up through the H_2 line and into the chamber, causing Ge deposition in the chamber. The HCl produced by the reaction between $GeCl_4$ and H_2 caused the molecular drag pump to cease functioning. The system was thereafter reconfigured to run at

atmospheric pressure. The H_2 purifier also ceased functioning at this point, possibly due to contamination of the palladium cell. The mechanical pump was also replaced at this point. The hydrogen purifier was taken out of the line, and the hydrogen was run through the oxygen remover only, and then directly into the MFC.

My second test was an attempt at actual epi growth. When the valve to the bubbler was opened, liquid GeCl_4 rushed into the tube. Evidently, the large flow of hydrogen entering the 10 slm MFC created a suction, pulling out the liquid GeCl_4 . After this occurrence, the gas lines were reconfigured to bubble with He gas, so that the bubbling would be independent of the downstream dilution with hydrogen (see Fig. 27).

Shortly thereafter, another major setback occurred, which required the major part of the summer of 1990 to rectify. The RF power supply was turned on, although the cooling water to the laboratory building had been (unknown to me) turned off. This caused the solder on the oscillator tube to melt, and resulted in a flood. Several electrical shorts occurred as a result, two of the rectifiers were damaged, and melting took place in three of the Variacs. Fuses were installed to prevent this from happening to the Variacs in the future. A defective flow switch on the RF power supply was replaced.

After these problems were corrected, several growth attempts were carried out. These are described in detail in Table 3.

2.3.4.3. Results and discussion of growth attempts using GeCl_4

In growth #1, an 800°C H_2 pre-bake was used, followed by deposition at 750°C , with a $\text{GeCl}_4:\text{H}_2$ mole fraction of 6.8×10^{-3} . This resulted in $8\text{ }\mu\text{m}$ of film growth, but the layer was unfortunately not single crystal (see Fig. 28a). I then decide to examine the quality of the wafer surface after a hydrogen pre-bake step,

XBL 913-4779

Fig. 27. Gas manifold for epitaxial runs using GeCl_4 as the germanium precursor. Bubbling is carried out with He; H_2 is used as the carrier gas downstream.

Table 3. Growth runs using GeCl_4

Crystal No.	Substrate conc. (cm^{-3})	Mole fraction GeCl_4	Growth temperature	$\text{H}_2:\text{GeCl}_4$ flow setting	Film thickness	Surface appearance
1) 736	Ge:P (100) $[\text{P}] = 1.8 \times 10^{14}$	6.8×10^{-3}	750 °C 800 °C H_2 bake	10.84/1.48	8 μm	very rough
2) 736	Ge:P (100) $[\text{P}] = 1.8 \times 10^{14}$		15 min H_2 bake at 820 °C		no change in wt.	preferentially etched
3) 736	Ge:P (100) $[\text{P}] = 1.8 \times 10^{14}$		15 min. vac. bake at 870 °C; syton polish		Ge redeposited from graphite	very opaque
4) 736	Ge:P (100) $[\text{P}] = 1.8 \times 10^{14}$	1.8×10^{-4}	750 °C; syton polish ramp up in H_2	10.84/0.40	5000 Å	very poor
5) 742	Ge:Ga (100) $[\text{Ga}] = 1.5 \times 10^{13}$		750 °C / H_2 only "mock dep"; polish etched ramp up in H_2			streaky, hazy
6) 742	Ge:Ga (100) $[\text{Ga}] = 1.5 \times 10^{13}$	6.8×10^{-3}	750 °C "real dep" ramp up in H_2 polish etched	10.84/1.49	no growth (bubbler empty)	spotty

Fig. 28. Optical micrographs from GeCl_4 growth attempts. [XBB 914-2749]

as compared to pre-bake in a vacuum. The surface of the wafer that was pre-baked in hydrogen showed preferential etching of residual scratches that were left over from the wafer polishing step. Dislocations can be observed nucleating from these scratches (see Fig. 28b). Although the sample was preferentially etched by hydrogen, there was no measurable weight change in the sample. In an attempt to improve the surface quality, the surface of the next sample (#3) was manually rubbed on the polishing pad with the $\text{H}_2\text{O}/\text{syton}/\text{H}_2\text{O}_2$ (6:3:1) mixture that is used in the final stage of polishing. The surface appeared to be of much higher quality under the optical microscope, although some scratches were still visible. This sample was then pre-baked in a vacuum at 870°C . The surface appeared opaque to the eye, and it seemed as if Ge from the graphite susceptor had evaporated and then redeposited on the wafer surface.

Since both of the pre-deposition bake techniques resulted in a surface of poor quality, it was decided to carry out a run without this step. In all subsequent growth attempts, I simply ramped up the growth temperature in H_2 , and began deposition. In run #4, the sample received a syton polish, followed by deposition at 750°C , with a 1.8×10^{-4} mole fraction. This resulted in a polycrystalline film growth of about $5000 \text{ \AA}$ (see Fig. 28c).

In order not to unnecessarily waste the hard-to-prepare optically-flat polished samples, it was decided to experiment with polish-etched cut slices. This etching procedure involves a 3:1 ratio of $\text{HNO}_3:\text{HF}$, and etches at about $0.5 \mu\text{m}/\text{min}$. The surface is left very smooth, although not optically flat. In principle, this should not interfere with epitaxial growth, and allowed the optically flat surfaces to be saved for Hall effect samples and BIB detectors. It was found that an etch time of 2 minutes was optimal for achieving a smooth surface. Runs #5 and 6 were done on polish-etched samples. In run #5 a "mock-deposition" was run, in which H_2 was run at 750°C without turning on the GeCl_4 . The procedure was identical for

sample #6, except that the GeCl_4 was turned on. Sample #5 appeared streaked and hazy to the eye, and revealed many dislocations when examined under the optical microscope (see Fig. 28d). The surface quality on sample #6 was also very poor (see Fig. 28e), and there was no measurable weight gain for the sample. I subsequently concluded that the bubbler was empty, and testing was stopped until the bubbler could be refilled with GeCl_4 by Eagle-Picher.

It is well-known that the presence of water vapor has very deleterious effects on quality of silicon epitaxial layers. It has been found by ASM Epitaxy in Tempe, Arizona [74] that bypassing the hydrogen purifier resulted in an immediate transition from single crystal to polycrystalline films. Douglas Meyer of ASM Epitaxy claims that a H_2O concentration exceeding 1 ppm in the hydrogen gas will lead to the growth of polycrystalline films [75]. Meyer also found that, without the purifier, the growth rate decreased by almost 30%.

Since all of my test runs with GeCl_4 were carried out without the use of the hydrogen purifier, the hydrogen gas therefore contained about 3.5 ppm water vapor, as stated in the Airco purity specifications for hydrogen. In addition, there was a concentration of about 10 ppm of other impurities, excluding helium. It is felt that this was a major impediment to the successful growth of epitaxial films.

3. GERMANIUM BIB DETECTORS

As mentioned in section 2.3.3.3, germanium substrate samples were sent to Mike Timmons at the Research Triangle Institute in Research Triangle Park, N.C. His lab was running a germane GeH_4 epi process, and was obtaining epi layers with background concentrations of $10^{14} - 10^{15} / \text{cm}^3$, with dopant profiles of a few tenths of a micron. Although the purity of their epi-layers was not nearly sufficient for use as BIB detectors, I felt that sending them some samples was worth a try. Both p-type and n-type samples were sent. The p-type samples, which were intended for

BIB detector fabrication, had 1 μm and 3 μm epi-layers grown on them. The n-type samples had 1 μm , 3 μm and 5 μm layers grown on them, and were intended for SIMS analysis and Hall effect measurements.

All of the layers were grown at 725°C, and at a reactor pressure of 150 Torr. The hydrogen carrier flowrate was 10 l/min. The growth rate for the samples was about 0.13 $\mu\text{m}/\text{min}$. Spreading-resistance profiles of layers grown under these conditions indicated p-type material with background carrier concentrations of about 10^{14} – $10^{15}/\text{cm}^3$. A light etch before loading the wafers into the reactor revealed work damage that probably remained from the polishing.

3.1. BIB Detector Fabrication

BIB detectors were fabricated from the 1 μm and 3 μm epi layers grown on p-type, Ge:Ga (100), $1.5 \times 10^{16}/\text{cm}^3$ substrates. Both sides of the samples were implanted with boron at a dose of $2 \times 10^{13}/\text{cm}^2$, and at an energy of 25 keV. This implant procedure produces ohmic, semi-transparent contacts [76]. 2 mm $\times$ 2 mm square samples were then cut with a dicing saw. The cut edges were polish-etched. Etching removes any damage created by the sawing, and passivates the surface, to prevent any adverse leakage currents. Indium solder was then used to attach a strip of copper to the bottom substrate surface of the detector. The specimens were then mounted on copper heat sinks, and placed in an integrating cavity that fit into the cryogenic test dewar. A copper wire was pressure-welded to the top epi-surface, using a pure indium pad.

3.2. Important Detector Parameters

Infrared detectors used in low-background conditions are characterized by three basic parameters, the responsivity, the dark current, and the noise-equivalent-power. The responsivity, which indicates the spectral range over which the detector

operates, is defined by

$$R = (e/h\nu)G\eta , \quad (5)$$

where e is the charge on an electron, h is Planck's constant, ν is the frequency of the incident photon signal, η is the quantum efficiency (i.e., the fraction of incident photons that are absorbed), and G is the detector gain. The detector gain can be expressed as

$$G = V_d t / L , \quad (6)$$

where V_d is the drift velocity under a given field, t is the carrier lifetime, and L is the interelectrode distance. Thus, the responsivity is expressed in units of A/W, where the output signal of the detector is measurable in Amperes, and the incident photon signal is measured in Watts.

The dark current, measured in Amperes, is defined as the current that flows through the detector in the absence of incident photons. In a BIB detector, dark current is primarily caused by thermally-generated free carriers from the heavily-doped layer.

The noise-equivalent power (NEP) is a measure of the smallest amount of radiant power that can be detected. It is a measure of the signal-to-noise ratio, relative to the incident photon power, and is therefore an indicator of the sensitivity of the detector. It is defined as

$$NEP = PN/S , \quad (7)$$

where P is the incident photon signal power, measured in Watts, N is the background noise of the detector in units of A/Hz^{1/2}, and S is the detector output signal, measured in Amperes. NEP therefore is measured in units of W/Hz^{1/2}.

3.3. Detector Results from Epi Layers Grown at Research Triangle Institute

The first detector tested had 3 μm of epitaxial film. With the 99 μm filter, this detector gave no signal. A black poly-filter was used in the next test, which will detect signals from all wavelengths greater than 60 μm , and should therefore increase the signal. The signal did increase from about 25 μV to 3.8 mV, at 1.5 K. Since it was impossible to know the wavelength that this signal was due to, we decided to use the Fourier Transform Spectrometer to obtain a plot of response vs. wavelength. The signal from the detector was too weak to produce a meaningful spectrum.

A second detector was made from the 1 μm thick epi layer. It was thought that the thinner epi layer might help, if too much bias voltage drop had been occurring in the 3 μm epi layer, and not in the substrate. This detector showed a signal with the 99 μm filter, although the leakage was high. The detector was tested with the Fourier Transform Spectrometer and showed an extended spectrum, but it appeared essentially the same under both negative and positive biases, and seemed to be acting like a conventional detector. The boron-implanted regions may have been the source of the spectral response. Figs. 29-31 show plots of the responsivity, NEP, and dark current for this detector.

This detector did not exhibit figures of merit required for low-background applications. The far-infrared space-based astronomy application limitations for dark current are less than 100 electrons/sec/pixel, with a typical pixel size of less than $0.5 \times 0.5 \text{ mm}^2$ [77]. Since our detectors were $2 \text{ mm} \times 2 \text{ mm}$, it can be seen from Fig. 31 that the dark current in our detector was too high by a factor of about 10^3 . It is not clear why the dark current is less under forward bias, and steadily decreasing as a function of the applied voltage. In a standard BIB detector, the dark current would be lower in the reverse-bias condition, indicating that the epitaxial layer was, indeed, blocking hopping conduction.

Fig. 29. Responsivity vs. bias for BIB detector made from sample with 1 μm thick epitaxial layer grown at the Research Triangle Institute. [XBL 914-749]

Fig. 30. NEP vs. bias for BIB detector made from sample with 1 μm thick epitaxial layer grown at the Research Triangle Institute. [XBL 914-748]

Fig. 31. Dark current vs. bias for BIB detector made from sample with 1 μm thick epitaxial layer grown at the Research Triangle Institute. [XBL 914-747]

Fig. 30 shows NEP values of about $7 \times 10^{-14} \text{ W/Hz}^{1/2}$ for the detector under reverse-bias conditions. This is about 100 times higher than in conventional detectors, and would be totally unacceptable in low-background conditions.

The responsivity, shown in Fig. 29, was the same under both forward and reverse biases. This indicates that the electric fields are the same under both biases, and that the detector is not functioning as a BIB detector. The sharp drop in responsivity under forward bias occurred at 80 mV, just prior to breakdown. The responsivity of this detector is 100–1000 times lower than that of a conventional Ge:Ga detector [78].

The spectral response, as a function of wavelength λ , for reverse and forward biases is shown in Figs. 32 and 33. Under reverse bias, the long-wavelength cutoff shifted from 160 to 190 μm when the applied bias was varied from -10 to -60 mV. Under forward bias, the long-wavelength cutoff is 190 μm , for applied biases ranging from +10 to +60 mV. This cutoff is significantly extended from that of a conventional gallium-doped germanium detector, which would be about 120 μm , at most [2]. The fact that the long-wavelength cutoff is approximately the same under both biases indicates that the detector is not functioning as a BIB detector, but more like a conventional detector.

The dopant concentration of the epitaxial layer grown at Research Triangle Park was about $10^{14} - 10^{15} / \text{cm}^3$, whereas the onset of hopping conduction occurs at approximately $10^{15} / \text{cm}^3$ [9]. We thus see that it is quite probable that hopping conduction was occurring in these layers, as the data suggest. Without a functioning blocking layer, the existence of large dark currents is not unexpected.

XBL 913-4776

Fig. 32. Spectral response vs. wavelength for detector under reverse bias.

XBL 913-4775

Fig. 33. Spectral response vs. wavelength for detector under forward bias.

4. CONCLUSIONS

(1) Various deposition techniques for growing germanium epitaxial layers have been investigated for the purposes of producing blocked impurity band (BIB) far-infrared radiation detectors.

(2) A low pressure chemical vapor deposition (LPCVD) process was developed, using GeH_4 gas as the germanium precursor. The layers contained a light residual copper contamination, as well as unacceptable levels of oxygen and carbon at the substrate/epi-layer interface.

(3) Growth attempts using a liquid source of tetramethylgermanium ($\text{Ge}(\text{CH}_3)_4$) proved to be unsuccessful, as the $\text{Ge}(\text{CH}_3)_4$ would not completely crack.

(4) Preliminary results using an atmospheric CVD process, with GeCl_4 , seem promising, although the epi-layer quality obtained with this procedure was poor, due to the presence of unacceptably high levels of water vapor in the hydrogen carrier gas.

(5) Detectors that were fabricated from epitaxial layers grown at Research Triangle Park displayed very poor values of responsivity, NEP, and dark current. This can be attributed to the high background concentration in the epi-layers, which prevented them from functioning as blocking layers.

(6) Major system modifications were made during the course of this work, to allow for direct loading of the sample from the cleaning area to the deposition system, while maintaining the sample under laminar flow in order to reduce the number of particulates accumulating on the wafer surface during loading of the sample.

(7) I strongly feel that high-purity epi-layers will not be obtainable with the present apparatus, until a high-temperature hydrochloric acid (HCl) *in situ* cleaning step is incorporated into the deposition process. This is the only way to obtain the damage-free, carbon-free, and oxide-free surfaces that are crucial for high-quality

epitaxial growth.

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APPENDIX I. Calibration of Mass Flow Controllers

Example: Flowrate of TMGe through a GeH_4 MFC

Procedure:

1. Evacuate chamber and gas lines.
2. Close hi-vac valve.
3. Have manifold valves open, flow switch off, but set at full scale.
4. Turn flow switch on, and simultaneously start timer.
5. Let gas flow in for a time t (in minutes).
6. A certain mass of gas enters into the tube.
7. Read pressure P_1 on the Pirani gauge (in Torr).
8. From ideal gas law, $P_1 V_1 = nRT$, where V_1 is the actual volume of the gas.
9. If this gas were at 1 atm pressure, it would occupy some volume V_o , where $V_o = nRT/P_o$, where $P_o = 1 \text{ atm} = 760 \text{ Torr}$, and V_o is the volume at STP.
10. Therefore $P_o V_o = P_1 V_1$, hence $V_o = P_1 V_1 / P_o$, where P_1 is measured on the Pirani gauge, and V_1 is the volume of the tube.
11. The flowrate at STP is $\dot{Q} = V_o / t$, where V_o is the volume (in cm^3) at STP, and t is the time (in minutes). $\dot{Q}$ is then measured in standard cubic centimeters per minute (sccm), and in this example is the flowrate of the TMGe.
12. Compare this flowrate to the nominal flowrate for GeH_4 , for which the MFC is calibrated (full scale = 20 sccm).
13. Verify technique by checking the flowrate of He through the He MFC.

APPENDIX II. Growth Parameter Calculations

One method for transporting a chemical to the process reactor in the vapor phase is known as "bubbling" (see Fig. 34). This procedure involves passing a carrier gas through a liquid source of the chemical to be delivered to the reactor. As bubbles of carrier gas rise through the liquid source, some of the liquid diffuses into the bubble in the vapor phase, and is transported with the carrier gas to the reactor. The mechanism for this process is that the source chemical will have a very low partial pressure in the bubbles, which initially are mainly comprised of the carrier gas, and so some of the liquid will vaporize at the surface of the bubble, and enter the bubble in the vapor phase.

If the carrier gas is passed through a liquid chemical source at constant temperature, it is desirable to introduce the gas slowly, so that the gas bubbles have time to equilibrate (thermally and thermodynamically) with the liquid. Under optimal conditions, the bubbles become fully saturated with the gas phase of the source liquid, and there is chemical equilibrium between the gaseous and liquid phases of the source chemical. Under these conditions, the amount of source material in the bubbles will be maximized.

Assuming full saturation and thermal equilibrium, the mass ratios of gases in each bubble should be the same. Therefore, if we assume that the gas inside the bubble obeys the ideal gas law, we can describe the mass flowrate of GeCl_4 as follows:

$$\dot{Q}_{\text{GeCl}_4}^{\text{bubbler}} = \dot{Q}_{\text{H}_2}^{\text{bubbler}} \left[\frac{P_{\text{GeCl}_4}^{\text{vapor}}}{P_{\text{H}_2}^{\text{tank}} - P_{\text{GeCl}_4}^{\text{vapor}}} \right],$$

where

Fig. 34. Schematic diagram of a bubbler. [XBL 914-746]

$$P_{H_2}^{\text{tank}} = 5 \text{ psig} = 14.7 + 5 = 19.7 \text{ psia} ,$$

$$P_{GeCl_4}^{\text{vapor}}(20^\circ\text{C}) = 76 \text{ Torr} = 1.47 \text{ psia} .$$

Therefore,

$$\dot{Q}_{GeCl_4}^{\text{bubbler}} = \dot{Q}_{H_2}^{\text{bubbler}} \left[\frac{1.47}{19.7 - 1.47} \right] = 0.081 \dot{Q}_{H_2}^{\text{bubbler}} .$$

If we want a mole fraction of 10^{-3} ,

$$\frac{\dot{Q}_{GeCl_4}^{\text{bubbler}}}{\dot{Q}_{H_2}^{\text{total}}} = \frac{0.081 \dot{Q}_{H_2}^{\text{bubbler}}}{\dot{Q}_{H_2}^{\text{bubbler}} + \dot{Q}_{H_2}^{\text{carrier}}} = 10^{-3} ,$$

So

$$0.081 \dot{Q}_{H_2}^{\text{bubbler}} = 10^{-3} \dot{Q}_{H_2}^{\text{bubbler}} + 10^{-3} \dot{Q}_{H_2}^{\text{carrier}} .$$

The first term on the right of the above equation is negligible compared to the second. so

$$\dot{Q}_{H_2}^{\text{bubbler}} \approx \frac{10^{-3}}{0.081} \dot{Q}_{H_2}^{\text{carrier}} = 0.0123 \dot{Q}_{H_2}^{\text{carrier}} .$$

If we run the carrier gas at maximum flow,

$$\dot{Q}_{H_2}^{\text{carrier}} = 10 \text{ slm} ,$$

$$\dot{Q}_{H_2}^{\text{bubbler}} = 0.0123(10,000 \text{ sccm}) = 123.4 \text{ sccm} .$$

Now,

$$\dot{Q}_{\text{total}}^{\text{bubbler}} = \dot{Q}_{H_2}^{\text{bubbler}} + \dot{Q}_{\text{GeCl}_4}^{\text{bubbler}} ,$$

but,

$$\dot{Q}_{\text{GeCl}_4}^{\text{bubbler}} = 0.081 \dot{Q}_{H_2}^{\text{bubbler}} .$$

So,

$$\dot{Q}_{\text{total}}^{\text{bubbler}} = \dot{Q}_{H_2}^{\text{bubbler}} + 0.081 \dot{Q}_{H_2}^{\text{bubbler}}$$

$$= 1.081 \dot{Q}_{H_2}^{\text{bubbler}} = 1.081(123.4) = 133.5 \text{ sccm} .$$

Since the fully opened position on MFC #3 is 1000 sccm, it is desired to operate at $133.5/1000=13.4\%$ of full scale. (13.4% of 11.15=1.49, with MFC #1 fully opened). To obtain a mole fraction of 10^{-4} ($\text{GeCl}_4:\text{H}_2$), we would run MFC #3 at roughly 0.15 (which is approximately the controllable limit of the MFC), and also

run MFC #1 at 100%.

At atmospheric total pressure, the partial pressure of the GeCl_4 is $0.081/1.081 = 0.075 = 7.5\%$, coming out of the bubbler. The GeCl_4 partial pressure in the tube is about $10^{-3} - 10^{-4}$ atm.

The second issue to be considered is the feasibility of achieving the hydrogen flow velocities that Rockwell used (10–20 cm/sec) in our chamber. The flowrate $\dot{Q}$ is given by

$$\dot{Q} = VA,$$

where V is the velocity with dimensions of [length/time], and A is the area with dimensions of [length²]. So $\dot{Q}$ is the flowrate with dimensions of [length³/time].

Now

$$A = \frac{\pi D^2}{4} = \frac{\pi}{4} \left[(2\text{in})(2.54\text{ cm/in}) \right]^2 = 20.27\text{ cm}^2 .$$

If $V = 10\text{ cm/sec}$, then

$$\dot{Q} = \left[\frac{10\text{ cm}}{\text{sec}} \right] (20.27\text{ cm}^2) = 202.7\text{ cm}^3/\text{sec}$$

$$= 12161\text{ cm}^3/\text{min} = 12.16\text{ slm (H}_2\text{)} .$$

If $V = 20\text{ cm/sec}$, then

$$\dot{Q} = 24.32 \text{ slm (H}_2\text{)} .$$

Now, given that the maximum hydrogen flow rate for MFC #1 is 10 slm,

$$V_{\max} = \frac{100}{12.16} = 8.22 \text{ cm/sec}$$

in our tube. Flowing through the hydrogen purifier with maximum output of 5 slm, we then have

$$V_{\max} \approx 4 \text{ cm/sec} .$$

APPENDIX III. System Schematics

See schematic diagrams on following pages.

EPI Rig Modification Loading Tube Extension

Body Piece - A

XBL 913-4768

Body Piece-B

XBL 913-4772

Inner Sleeve

XBL 913-4770

Squash Ring

XBL 913-4774

FlangeTo Pump

XBL 913-4769

End Flange

XBL 913-4771

XBL 913-4767

END

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12 / 16 / 91