Gallium-Doped Silicon Blocked-Impurity-Band Detectors

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ABSTRACT

Boeing and Lawrence Semiconductor Research Laboratory are developing high-performance gallium-doped-silicon (Si:Ga) impurity-band-conduction material and Blocked-Impurity-Band (BIB) detectors. We build on a strong technology base in arsenic-doped silicon (Si:As) material and BIB detector technology. Si:As large-format focal plane arrays offer background-limited infrared performance (~28 µm cut-off wavelength) and excellent pixel operability and uniformity to many defense and space imaging and spectroscopy applications. Application of Si:As BIB detectors to long-lifetime missions is restricted by operating temperature (~10 K) below the range of available cooler technologies. The development of a Si:Ga option, with several degrees higher operating temperature, is intended to ease this restriction. The Si:Ga cut-off wavelength (~18 to 20 µm) is suitable for many ground- and space-based applications. Known Si:Ga material development issues have been circumvented and detector-quality Si:Ga material and initial front- and back-illuminated BIB detector structures have been prepared and evaluated. We report dark current, quantum yield, and spectral response for prototype devices and discuss material and detector improvement directions.

1. INTRODUCTION

Blocked-Impurity-Band (BIB) detectors were invented\(^1\)\(^2\) by Petroff and Stapelbroek in the early 1980’s while addressing debris-gamma hardening of infrared detectors for space surveillance missions. Focal plane arrays (FPA) of arsenic-doped silicon (Si:As) BIB detectors soon followed, with the development of back-illuminated BIB arrays, matching readout multiplexers, and techniques for hybridizing these


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components. Array formats have grown to 1024x1024 elements. Si:As BIB detector material has been highly developed by Boeing and others for applications covering a wide range of environments, from very low flux (space-based infrared imaging and spectroscopy) to very high flux (high-altitude missile interceptors). While less highly developed, BIB detectors have also been made using antimony, phosphorus, boron, and gallium.

Si:As provides infrared sensitivity to a cut-off wavelength of 27 to 30 microns, depending on the dopant concentration used. Practical limits on operating temperature for Si:As BIB detectors lie between 8 and 14 K, set by doping concentration range and dark current requirements. Since the early years of BIB detector development, it has been understood that a material with somewhat wider impurity band gap, such as Si:Ga would be a better match for ground-based or low-altitude applications. Operating temperature would be increased by several degrees, easing the burden on cooler technologies, and cut-off wavelength would be reduced to a value better matched to atmospheric windows. Si:Ga BIB detector development was pursued prior to 1987 using float-zoned Si:Ga material. Back-illuminated BIB detectors and hybrid focal plane arrays were achieved and evaluated. Low, non-uniform gallium concentration for the float-zoned material led to poor frequency response and non-uniform arrays.

Recent interest from NASA has spurred a reexamination of the prospects for high-performance Si:Ga BIB detectors. NASA’s Origins missions, to be sited in high-earth orbit or beyond, will require mid-infrared detectors sensitive to wavelengths of at least 10 µm (up to 20 µm for spectroscopy of planets around nearby stars to identify Earth-like atmospheres). Operating temperatures have to be compatible with long-lifetime coolers being developed concurrently. Unfortunately, the lowest temperatures expected to be achieved by these coolers (~10 K) does not provide design margin for use with very-low-flux Si:As BIB detectors. Si:Ga BIB detectors, operating several degrees warmer than Si:As, would be easily accommodated.

Under NASA contracts Boeing and Lawrence Semiconductor Research Laboratory (LSRL) have proceeded with a reexamination of Si:Ga BIB detector development. We have made excellent progress in demonstrating the potential for high-performance BIB detectors by leveraging the highly developed Si:As BIB detector infrastructure and improvements in the purity of silicon and gallium source gases over the past decade.

### 2. MATERIAL DEVELOPMENT

#### 2.1. Semiconductor Epitaxial Growth Facility

LSRL is a premier supplier of custom Group IV layer depositions. Boeing and LSRL have an exclusive relationship for the development and small-scale production of silicon BIB detector layers (epitaxy) to meet increasingly challenging requirements of defense and space applications. LSRL currently operates four radiant-heat single-wafer chemical vapor deposition (CVD) reactors with custom source- and dopant-gas systems. Substrate and product wafers are prepared and handled in an industry-standard cleanroom.

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6 NASA/JPL Contract 958325.

7 NASA/ARC Contract NAS2-98076.
By great attention to impurity backgrounds, layer interfaces, and factors that affect crystal quality, LSRL has routinely provided Boeing with Si:As BIB detector epitaxy of excellent quality. A very wide range of epitaxy designs has been realized, suitable for very high flux to very low flux applications.

2.2. Gallium Source and Silicon Doping Chemistry

Many years ago Rai-Choudhury\(^8\) made an initial attempt at doping silicon with gallium using the organometallic source trimethylgallium \(\text{Ga(CH}_3\text{)}_3\). Although gallium doping was achieved, the crystalline quality of the layer was inferior, likely due to high levels of carbon incorporated during the doping. The residual donor concentration in these layers was not measured. More recently Huffman\(^9\) attempted the growth of Si:Ga using gallium trichloride. Although higher purity layers were achieved, the doping source was difficult to use, and the gallium concentration was limited to about \(1 \times 10^{17} \text{ cm}^{-3}\) -- too low for BIB detector applications.

The III-V semiconductor industry has recently made extensive use of organometallic sources, notably trimethyl- and triethylgallium \(\text{Ga(C}_2\text{H}_5\text{)}_3\). Their importance for GaAs and GaN growth has led the source material suppliers to significantly increase the source purity using adduct purification. The increased purity led us to believe that either of these sources would be suitable for preparing high-purity Si:Ga epitaxial layers for BIB detector applications. Triethylgallium was considered best suited to this application and the source and ancillary delivery system were obtained and used.

The growth of high-purity Si:Ga epitaxial layers also requires a high-purity silicon source. Since gallium is a p-type dopant in silicon, donor impurities are of central concern. Based on our experience with Si:As development and general performance models, the minority impurity concentration should be less than \(5 \times 10^{12} \text{ cm}^{-3}\) for high-performance BIB devices. Typical donor impurities in the silicon source include arsenic, phosphorus and antimony. Options for silicon sources include silane and dichlorosilane. Both are known to be capable of producing unintentionally doped silicon epitaxy with net carrier concentrations less than \(5 \times 10^{12} \text{ cm}^{-3}\). Commercially available trichlorosilane is not a candidate source, as it tends to provide silicon layers with n-type impurity net carrier concentration \(\sim 10^{13} \text{ cm}^{-3}\). Initial test runs were used to evaluate silane and dichlorosilane by growing 20 µm of undoped silicon epitaxy on lightly doped silicon substrates. Net carrier concentrations by spreading resistance analysis confirmed that both silicon sources are of sufficient purity for this application.

The doping chemistry will depend on the silicon source used. Potential reactant pathways for the decomposition of the silicon source and triethylgallium include:

\[
\begin{align*}
2\text{SiH}_2\text{Cl}_2 + 2\text{Ga(C}_2\text{H}_5\text{)}_3 & \rightarrow 2\text{Si:Ga (s)} + 4\text{HCl(g)} + 3\text{C}_2\text{H}_6(g) + 6\text{H}_2(g) \quad \text{(Dichlorosilane)} \\
2\text{SiH}_4 + 2\text{Ga(C}_2\text{H}_5\text{)}_3 & \rightarrow 2\text{Si:Ga (s)} + 3\text{C}_2\text{H}_6(g) + 10\text{H}_2(g) \quad \text{(Silane)}
\end{align*}
\]

We made a series of test runs using triethylgallium with silane or dichlorosilane for Si:Ga epitaxial layers. These resulted in the selection of the silane growth chemistry for this work, based on the relative superiority of the gallium incorporation and crystal quality it provided.

2.3. Development Process

The Boeing-LSRL collaboration in Si:As BIB detector development for new applications and advancing requirements was the model for our development of Si:Ga BIB detectors. Initial layer parameter targets were set based on BIB detector models and design tools developed at Boeing over many years and LSRL’s detailed understanding of the science and technology of CVD. LSRL was able to bring prior


experience with gallium doping of silicon to bear to rapidly select the most promising approach for fabrication of specified detector structures. Gallium-doped test layers were prepared and evaluated both at LSRL and at Boeing, and initial BIB detector structures were prepared in August 1998. Three further development cycles in February, April, and June 1999 resulted in reduction of the background underlying the detector structure and fabrication of this structure on high-purity (infrared transparent) silicon substrates. This latter activity was non-trivial, since it required parallel development of a transparent contact on the substrate surface to be buried by the BIB epitaxy. Performance of both the contact and the overlying epitaxy had to be preserved in their joint application. Boron surface implantation was used for the initial buried contact, but direct contact experiments were successful and may be implemented in future development.

Epitaxy from each development cycles was evaluated at both LSRL and Boeing to verify that design goals were achieved. Then, Boeing performed more detailed analyses by fabrication and testing minimal detector structures. Data from the material evaluations and detector tests will be presented in the following sections.

2.4. Material Evaluation

2.4.1. Methods

Boeing and LSRL employ several material evaluation methods for BIB detector epitaxy. Spreading Resistance Analysis (SRA) is used routinely to calibrate or validate layer thickness and doping levels. Secondary Ion Mass Spectrometry (SIMS) is frequently applied to confirm SRA results and evaluate sharp layer transitions. Cryogenic Capacitance vs. Voltage Analysis (CCVA) is routinely applied to measurement of the minority dopant concentration in the doped silicon deposits. This background impurity concentration is the most significant material-quality indicator for BIB detectors, since it determines the bias voltage that must be applied to the BIB detector structure to achieve full quantum efficiency. High bias voltage has undesirable effects, such as impact ionization gain (a noise source) and blocking layer leakage after high-energy particle irradiation.

2.4.2. Si:Ga SRA Results

SRA is implemented at both at Boeing and LSRL with a system of hardware, software, and calibration and sample preparation methods provided by Solid State Measurements, Inc. of Pittsburgh, PA. A small rectangular bar sample (typically 1 mm x 3 mm) is removed from a wafer containing the epitaxy to be analyzed. One end of the bar is lapped at a shallow angle (~0.7 degree) to the surface to laterally expose material deposited at progressive depths within the epitaxy. A pair of closely spaced (~40 µm) probes is stepped down the lapped surface for measurement of spreading resistance at intervals corresponding to increasing depth in the epitaxial layer. System algorithms convert the resistance data vs. probe position to carrier-concentration vs. depth. At the low compensation levels in BIB detector material, carrier concentration is a direct measure of majority dopant concentration.

The SRA profiles for present Si:Ga BIB detector layers are shown in Fig. 1. The heavy solid and dashed profiles are for material prepared during 8/98 and 4/99 on degenerate and high purity (boron surface-implanted) substrates, respectively. The boron buried contact spike in the dashed curve at a depth of 15 µm appears broadened by the SRA depth resolution. Gallium concentration, in the region between 3 and 15 µm, is unintentionally graded in present depositions, but this depth non-uniformity will be removed in future development. Already, a thicker more uniform deposition (light curve) has been obtained but not yet evaluated for BIB detector performance.
LSRL employs SRA on reactor test samples to calibrate the silicon growth rate and dopant incorporation prior to batch growth of specified layers. Boeing subsequently applies SRA for certification of wafer batches by measuring the dopant profile for a representative wafer from the batch. The SRA systems at LSRL and Boeing have been successfully cross-compared, and targeted and achieved profiles are routinely in good agreement.

2.4.3. Si:Ga CCVA Results

The CCVA for minority impurity concentration requires a wafer sample with a minimal BIB detector layer structure, including the doped and undoped blocking layer. This sample must be cooled to the deep cryogenic temperature appropriate to the dopant species utilized. Typically the CV test samples are grown on degenerate substrates that provides a common back electrical contact. Top electrical contacts with well-defined areas are usually prepared by sputtering aluminum directly on the sample through a shadow mask that yields four detectors of 4-mm-diameter active area. For quick-turn-around CCVA at LSRL, circles of indium foil ~7 mm in diameter are melted onto the BIB wafer samples to define the detector area.

CCVA samples are usually tested in custom quick-turn-around cryostats that provide spring-loaded electrical contact to detector metalization. The cryostats are cooled by insertion into the gas volume above the liquid level in a standard liquid-helium storage tank. After cooling to operating temperature CCVA proceeds by incrementally applying operating bias to the detector structure and measuring its capacitance. The applied voltage progressively expels impurity band carriers from the region below the blocking layer, increasing capacitance. The capacitance measurement applies a low frequency, small-amplitude ripple voltage to the bias voltage and detects the resulting AC response with a lock-in amplifier. The capacitance data are converted to a minority-impurity-concentration depth plot by the straightforward application of electrostatics.

Figure 1. Carrier concentration depth profiles by SRA for developmental Si:Ga BIB detector structures.
Fig. 2 shows minority impurity concentration in the initial (8/98) and more recent (2/99) Si:Ga BIB detector structures as determined by CCVA. The later impurity concentration is reminiscent of early Si:As BIB detectors. The indicated depth excludes the blocking layer thickness. At the relatively high impurity concentration of 8/98 the test sample could not be fully depleted, but an indication of mid-layer background was obtained. CCVA uncertainties are relatively large both at low and high depletion values, so concentration values at intermediate depth are considered as most representative of material quality. Further improvement in background impurity concentration is anticipated and should result in improving Si:Ga BIB detector performance over time, as was the experience with Si:As BIB detector development.

![Figure 2. Background donor impurity concentration underlying developmental Si:Ga BIB detector structures, showing improvement between the initial and more recent material runs.](image)

3. DETECTOR EVALUATION

3.1. Test Structures

The ultimate test of new or improved detector material is to fabricate and evaluate detectors from it. In the case of BIB detectors, it is not necessary to invoke the full detector fabrication process to obtain test structures for measurement of the most basic performance parameters. Minimal detector structures, fabricated from <1 cm² wafer samples can be used. We routinely utilize tests on these “quickfab” structures to assure suitable detector performance from a given material run prior to committing the material to full lot processing.

The CCVA test devices described above are, in effect, blind BIB detectors. They may be used for detector dark-current evaluation but are not optimal for that purpose. CCVA device areas are large, for precision and accuracy of capacitance measurement, so they often overlie small crystalline defects that result in leakage currents not characteristic of thermally generated detector dark current. Also, the CCVA device provides only four candidate detectors for testing—too small a sample to inspire high confidence in the measurement results.
Three types of quickfab detectors were utilized for measurement of Si:Ga BIB detector performance parameters. These are illustrated in Fig. 3. Device A, fabricated on a degenerate (boron-doped) substrate, is prepared in identical fashion to the aluminum-sputtered CCVA sample, except that the sputter mask provides twelve to twenty-four nominal 1-mm-diameter detector areas. These are blind detectors, suitable only for dark current evaluation. For typical defect densities, few of the detectors overlie crystalline defects. (The number of defective detectors provides a rough estimate of the “hot pixel” count to be expected in finished arrays.) Testing many similar detectors provides high-confidence measurement results.

Device B is also fabricated on a degenerate substrate, but a patterned top-contact implant and small metal pad permit optical measurements by illumination through the unobscured portion of the top contact. Device C is processed from BIB detector layers grown on high-purity silicon wafers implanted (boron) to provide a buried transparent contact for through-substrate illumination. As for SRA samples, a shallow bevel is lapped at one edge of the sample to expose the buried layer for electrical contact. Top contacts for Device C are as for Device A.

### 3.2. Test Methods

Dark current, photoresponse, and spectral response were measured for Si:Ga quickfab devices packaged in 38-pin leaded chip carriers. Each chip carrier accommodated two 1 cm x 1 cm quickfab devices, each with their complement of ~12 active detector areas. Detector contacts were connected to carrier leads by wirebonding. For dark current and photoresponse testing, packaged devices were cooled to operating temperature in a liquid-nitrogen/liquid-helium reservoir dewar. The package mount provided a heater and calibrated temperature sensor for establishing and controlling device temperature. A liquid-helium cooled radiation shield enclosed the test package to reduce detectable optical background to <10⁸ cm⁻² s⁻¹. A carbon resistor, mounted behind a 10.6-µm narrow-bandpass filter in the radiation shield, provided the infrared source for photoresponse testing when heated by an applied current. This source was calibrated in a separate experiment using a Si:As detector with known photoresponse. For testing of back-illuminated type C detector the chip carrier was perforated, and detector active volumes were aligned over the carrier perforations. In this case, the package was mounted upside-down in the test dewar to admit illumination through the package perforations into the device active volumes.

![Figure 3. Quickfab device types. The detector material is shown in medium shading. Device features are not to relative scale. Electrical contact polarity and illumination directions are indicated.](image-url)
A Hewlett-Packard Model 4145 Semiconductor Parameter Analyzer with custom data acquisition software was used to measure detector current vs. applied bias (I-V curves) for operating temperature steps of 1 or 2 K. Starting (lowest) temperature was typically 13 to 14 K, where dark current could just be observed at maximum measurement sensitivity. Photoresponse curves, expressed as quantum yield (product of quantum efficiency and internal gain) were obtained by subtracting source-off from source-on I-V curves and dividing by the known flux, detector area, and electronic charge.

Spectral response testing was performed in a liquid helium flow cryostat, designed to accept the beam from a Nicolet Model 560 Fourier Transform Infrared (FTIR) spectrometer. The FTIR cryostat accepted the same test packages as used for dark current and photoresponse testing. The FTIR spectrometer's thermal spectrum was obtained in a separate experiment utilizing a pyroelectric detector with calibrated wavelength response over the infrared region of interest.

### 3.3. Dark Current

Dark current measurements have been obtained for representative wafers from all Si:Ga material runs, using one or more quickfab types. Fig. 4 compares dark current I-V curves for devices made from the early (8/98) and most recent (6/99) Si:Ga material. Both data sets covered a range of operating temperature, as described in the figure legend. The data for 8/98 material (left panel) was from a type A quickfab detector, and the data for 6/99 material (right panel) was from a type C quickfab detector. With detectors of these types, there is a silicon-to-aluminum top-contact Schottky barrier to be overcome before detector current flows. This barrier is typically 0.3 to 0.6 V. Also, the test devices include no features to prevent hole injection from the back contact at high bias or surface leakage; therefore, current components associated with these or other effects are usually turn on at some bias voltage in the range of 1 to 2 V.

![Figure 4. Dark current vs. applied bias voltage and operating temperature for quickfab detectors of 0.8-mm² area. Left: Type A detector data from 8/99 Si:Ga material at 1 K temperature increments over indicated range. Right: Type C detector from 6/99 Si:Ga material; 2 K temperature increments.](image)

Dark current at a given effective bias voltage (applied bias minus turn-on threshold) was taken from the dark I-V data sets and analyzed for thermal activation characteristics. Fig. 5 is an Arrhenius plot including data from Fig. 4 and other data (dashed line) from a quickfab type B detector having 13 times the area of a type A or C detector. This type B detector was prepared from 8/98 Si:Ga BIB detector material. For comparison all currents were scaled to correspond to a typical array pixel size of 75 µm x
75 µm and expressed in units of electrons/s. The Si:Ga BIB detector dark current is consistent with thermally activation through mid-gap states from the gallium impurity band at about 72 meV. The two data sets from older detector material are in good agreement at higher temperatures, but the data from the larger detector has an anomalous current component that dominates at lower temperature. This current component probably arises from blocking layer leakage, due to one or more small crystalline defects underlying the large detector area.

The data from the most recent Si:Ga material were approximately an order of magnitude lower at given temperature than that from the older material. One reason for this difference is obvious: The data from 6/99 material was obtained at an effective bias of only 1 V (just below onset of a contact breakdown or leakage current component), while data from older material were obtained at an effective bias of 1.5 V. However, the apparent rate of change of current with bias (Fig. 4.) is not alone sufficient to account for the difference in current between devices from the two material groups. The relatively lower impurity background concentration of the newer material strongly contributes to the reduction in dark current. For given bias voltage, the maximum internal electric field in the BIB detector structure is a function of the background impurity concentration, and higher electric field assists the generation of dark current (Poole-Frenkel effect\textsuperscript{10}). The relatively larger value of the activation energy for the newer BIB detector structures is indicative of a reduced Poole-Frenkel effect.


\begin{figure}
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\includegraphics[width=\textwidth]{dark_current_graph.png}
\caption{Dark current temperature dependence for present Si:Ga detector structures. Legend includes fabrication date, type of quickfab device, and approximate operating bias voltage. Current is scaled to detector area of (75 µm)\textsuperscript{2}, typical of a focal plane array pixel.}
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3.4. Photoresponse

Two of the quickfab detector types (B and C) permit optical characterization of BIB detector structures. The initial BIB detector material, prepared only on degenerate (opaque) substrates, was evaluated with a type B device, which allows illumination through a transparent top contact. The most recent material, grown on a transparent buried contact layer, was evaluated with a type C device, which allows illumination through the transparent substrate. The differences in device structure are probably secondary to material impurity backgrounds in their effect on optical performance, and there are very large differences in optical performance.

Fig. 6 compares the 10.6-µm photoresponse data from the initial and recent Si:Ga material. Four curves, representing different operating temperatures (See figure legend.), are shown for each device. The photoresponse variation with temperature is small and typical of that seen in Si:As BIB detectors. The data for the type B device from initial Si:Ga material does not exhibit a turn-on potential barrier, since the top contact implant provides an ohmic contact; however, its quantum yield remains relatively low as bias is increased. This is probably due to the slow rate of depletion at the higher impurity backgrounds in this material. Optical absorption by the top contact implant also might be a significant factor reducing quantum yield.

![Figure 6](image_url)

**Figure 6.** Photoresponse results, expressed as quantum yield, from initial Si:Ga BIB detector layers processed with quickfab type B (8/98, B) and recent Si:Ga material processed with quickfab type C (6/99, C). Each data set includes four operating temperatures in 2 K increments. Curves for starting and beginning temperatures are indicated.

By contrast, the quantum yield for the recent Si:Ga BIB detector material, increases rapidly (after the silicon-aluminum Schottky barrier is overcome) to a value typical of fully-depleted response by 2 V. Beyond 2 V, dark current becomes much larger than photocurrent (See Fig. 4), making the determination of photocurrent by the difference method inaccurate.
3.5. Spectral Response

Spectral response data were obtained for the same quickfab devices as used for photoresponse measurements. Fig. 7 is a plot of the spectral response results. The response spectrum from 8/98 epitaxy was taken at 2.0 V bias and operating temperature of 13 K. It was relatively smooth, peaked near 12 µm with low total response, as discussed in the previous section. The spectrum for the 6/99 epitaxy, taken at 14 K and an applied bias voltage of 1.5 V, is peaked near 7 µm, but remains relatively flat over most of the spectral range. This result is consistent with the latter device, with its lower donor background, being almost fully depleted and offering a relatively larger detection length to short-wavelength radiation. The prominent oscillatory features seen in the 6/99 data are consistent in spacing and amplitude with channeling between the top metalization and buried electrical contact. (The spike seen near 9 µm is a measurement artifact due to electronic noise.)

![Figure 7. Spectral Response (wavelength dependence of quantum yield) for quickfab samples from initial (8/98) and recent (6/99) Si:Ga BIB detector material.](image)

4. CONCLUSIONS

The development of a BIB detector type with the excellent performance characteristics of Si:As BIB detectors, but operating several degrees warmer, would be applicable to long-lifetime space and defense surveillance missions. The application of gallium to BIB detectors for this purpose has been revisited with excellent progress. Our success is due in large part to improvements in the silicon CVD growth reactors and purity of silicon-source and dopant gases.

After evaluating options for the growth of Si:Ga material at dopant concentrations required for BIB detectors, initial device-quality BIB detector structures were prepared on degenerately doped (boron) substrates in August 1998. In follow-on development runs in the first half of 1999 material quality was greatly improved. Additionally, procedures for deposition of BIB detector layers on boron-surface-implanted, high-purity silicon wafers were developed, as needed for the fabrication of back illuminated BIB focal plane arrays (detector arrays flip-chip mated with read-out arrays).
Several types of quickfab devices have been successfully applied to the evaluation of Si:Ga BIB structures at the wafer level. These devices have been adequate for measurement of key detector performance parameters prior to full BIB detector lot fabrication. All data reported in this paper were obtained from such devices.

We plan to continue the evaluation of the most recent BIB detector structures and to further improve the material and layer design. Structures with thicker, more-uniformly-doped Si:Ga depositions have been demonstrated, and will be tested. A BIB detector process run will be carried out with Si:Ga layers near the present level of development. This run will provide detector arrays for focal plane array fabrication. Focal plane array testing will provide the most relevant performance evaluations as a guide to further improvements.

5. ACKNOWLEDGEMENTS

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