Arsenic-Doped Mid-Wavelength Infrared HgCdTe Photodiodes

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The recently developed Te-rich, liquid-phase-epitaxy growth technology for low arsenic-doped mid-wavelength infrared (MWIR) HgCdTe with p-type doping concentrations $<10^{15}$ cm⁻³ has enabled the fabrication of n⁺/p photodiodes using the damage associated with a boron ion implantation. The diode properties are presented and compared to similar diodes fabricated in p-HgCdTe doped with Group IBs. The attraction of the arsenic-doped diode technology is associated with the fact that the arsenic resides on the Te sublattice and is immune to the Hg interstitial fluxes that are present in the diode-formation process. This leads to minimal diode spread, limited primarily to the n⁺ region and, hence, a potential for use in really high-density infrared focal planes. At the same time, the Hg interstitials generated in the diode-formation process should purge the photodiode volume of fast diffusing species, resulting in a high-quality, diode-depletion region devoid of many Shockley–Read recombination centers. These aspects of diode formation in this material are discussed.

Key words: HgCdTe, As-doped, photodiodes, mid-wavelength infrared (MWIR)

INTRODUCTION

High-density, vertically integrated photodiode (HDVIP), infrared focal plane arrays have been fabricated at DRS Infrared Technologies (DRS, Dallas, TX) for a number of years using Group IBs counter-doped with a low background concentration of indium, as extrinsic dopants in an $n^{+}/n^{-}/p$ diode architecture. This diode geometry is shown in Fig. 1. The diode-formation process involves the formation of a via through the HgCdTe by ion etching/implantation down to the underlying silicon readout integrated circuit. The damage generated by the via process generates Hg interstitials that both fill Hg vacancies and displace Group IB dopants from the metal sublattice, resulting in the formation of an n⁻ region associated with the background indium concentration. The extrinsic dopant level and the damage rate of the etch/implant together determine the resulting diode spread. Issues of excessive diode spreading arise in system applications that require low dark currents (and, hence, low extrinsic/vacancy doping levels) and extremely high pixel densities.

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One possible technological approach that can circumvent these issues is the use of arsenic as the extrinsic dopant. Acceptor-activated arsenic resides on the Te sublattice and as such should be relatively immune to Hg interstitials. The possibility thus exists to form n^+/p diodes in HgCdTe in which the diode spread is limited to the n^+ region associated with the etch/implant, known to be $\sim 1-1.5$ -µm wide. This paper describes initial experiments aimed at reducing this potentially useful technology to practice and compares the resulting diodes to diodes fabricated in Group IB-doped material.

EXTRINSIC DOPING WITH GROUP IBs

Early HDVIP arrays were fabricated on vacancydoped, p-type HgCdTe counter-doped with indium at a level of $1-5 \times 10^{14}$ cm⁻³. Vacancy concentrations were typically in the $2-5 \times 10^{16}$ cm⁻³ range. The diode-formation process in this material thus involved a simple filling of metal vacancies with the damage-generated Hg interstitials. An added degree of complexity was introduced by doping with Group IB impurities. The purpose was twofold. The introduction of Group IB dopants allowed for a reduction in diode spreading and a reduction in vacancy



Fig. 1. Basic $n^+/n^-/p$ HDVIP architecture.

levels, with a subsequent reduction in dark current from the p-volume of the diode. The diode-formation process is shown in Fig. 2 for HgCdTe material doped with both Group IB extrinsic and vacancy acceptors and counter-doped with indium. The Hg interstitials generated by the etch/implant process both fill metal vacancies and displace Group IBs from the metal lattice sites, forming an n⁻ region because of the background indium level. The diode is thus an $n^+/n^-/p$ architecture. The purpose of the damage region is twofold. It not only acts as a source of Hg interstitials for diode formation but also provides a sink for the excess Group IBs displaced from the metal sublattice. Some of the displaced Group IBs can also diffuse ahead of the n^{-}/p front to fill vacancies, leading to a reduction in dark current from that particular part of the p-volume. The secondary ion mass spectrometry (SIMS) profile of Au in an HgCdTe slice that is doped with $\sim 6 imes 10^{15} \, \mathrm{cm^{-3}} \, \mathrm{Au}$ and $1.4 \times 10^{15} \ {
m cm^{-3}}$ vacancies and subjected to a 6×10^{14} /cm², 150-keV boron implant is included in Fig. 2, indicating a gettering of Au to the implant damage region. It should be pointed out that the SIMS profiling technique uses an ion etching process that does generate damage and, hence, Hg interstitials, which will tend to disturb the very Au profile that it is trying to measure. The resulting profile is thus a convoluted one because of both the profiling technique and the ion implantation. A comparison of the SIMS profile of Au for the implanted case versus the unimplanted case is shown in Fig. 3. The profile in the unimplanted case is seen to be



softer, and the gettering of Au to the front surface region is greatly reduced because of the much lower damage associated with the profiling etch. This phenomenon is treated more fully in the paper by Wang et al.¹

A band diagram of the resulting $n^+/n^-/p$ structure is also included in Fig. 2, illustrating that the depletion region of the diode is located entirely in the n-type region of the device. This is a region that has been purged by the Hg interstitials and, as a result, will be relatively devoid of any fast diffusing impurities and, hence, possibly purer. It is interesting to note that depletion currents are not typically observed in HgCdTe HDVIP devices at any temperature.

A set of current-voltage (I-V) curves as a function of temperature are shown in Fig. 4 for HDVIP diodes fabricated on mid-wavelength infrared (MWIR) (5.2-µm cutoff at 77 K) Au-doped material that is essentially the same as that profiled by SIMS in Fig. 2. The HgCdTe was \sim 9-µm thick and passivated with CdTe. The active diodes were surrounded by guard diodes that were reverse-biased at 200 mV. The geometry of a typical diode set is shown in Fig. 5. The active diode consists of the inner 2×2 matrix of individual HDVIP diodes surrounded by the outer diodes of a 4×4 matrix, which are connected together to form a guard diode. The test bar allows for diodes with varying pitch and via diameter. The diodes in Figs. 4 and 8 are, in fact, fabricated on a 40-µm pitch with 8-µm via diameters. The I-Vs contain idiosyncrasies that are symptomatic of the



Fig. 2. The HDVIP diode-formation process in Group IB extrinsically doped, MWIR (5.2 μm at 77 K) HgCdTe, indicating (a) impurity profiles, (b) band diagram of the structure, and (c) the SIMS profile of Au in boron-implanted, Au-doped HgCdTe.



Fig. 3. The SIMS profiles of Au in unimplanted and implanted MWIR HgCdTe illustrating the effect of the profiling etch used in SIMS on Group IB impurities in HgCdTe.



Fig. 4. The I-V characteristics of an HDVIP, n⁺/n⁻/p, Au-doped MWIR (5.2 μ m at 77 K) HgCdTe test diode at various temperatures. The n⁺ of the diode and guard diode are biased positive relative to the p-substrate in reverse bias. The modulus of the forward-bias current is plotted for convenience.

unit-cell geometry used and can be explained as follows:

- The zero offset of the I-V curves is due partly to long diffusion length effects between the diode and guard diode and partly due to substrate resistance and substrate contact issues that lead to a de-biasing of both the guard and active diodes at high dark currents. Both effects tend to forward bias the active diode at what should be low reverse-bias voltages.
- The dark current through the guard diode at high temperatures is large enough that it leads to almost total de-biasing of the 200 mV across the guard diode, resulting in a loss of the guard effect and a subsequent increase in the observed diffusion current.
- At low temperatures (<130 K), the dark currents are too low for the instrumentation used and should be ignored.
- Although not shown in Fig. 5, diode shunting was observed in diodes that were fabricated with a small pitch (i.e., high density) that also had large via diameters.

The dark currents are well behaved and diffusion-like over most of the indicated temperature range, as shown in Fig. 6, where they are compared to a modeled diffusion current for this HgCdTe composition.

EXTRINSIC DOPING WITH ARSENIC

Arsenic-doped HgCdTe has been grown^{2,3} at DRS with concentrations of $<10^{15}$ cm⁻³ using a Terich melt. The minority carrier lifetime at 77 K is state-of-the-art, as indicated in Fig. 7, for the MWIR material. Also included in Fig. 7 is state-of-the-art data for Au-doped material for both MWIR and long wavelength infrared (LWIR) HgCdTe. The lifetimes were measured using a contactless microwavereflectance technique⁴ to monitor the response of the conductivity of the HgCdTe material to an IR emitter



Fig. 5. Geometry of the diode and guard diode unit cell.



Fig. 6. Modeled diffusion current versus temperature for MWIR (5.2 μ m at 77 K) compared to the experimental data of Fig. 4, with Au at 7 \times 10¹⁵ cm⁻³ and vacancies at 1.4 \times 10¹⁵ cm⁻³.

pulse. The theoretical lines represent a combination of a Shockley-Reed (S-R) limited lifetime via an intrinsic energy level, and Auger7. The expressions for these components in p-type HgCdTe are given by⁵

$$\tau_{ext} = 9.1 \times 10^9 [n_i + p + N_a (n_i / (n_i + p))] / p N_a. \quad (1)$$

$$\tau_{\rm Al} = 2\tau_{\rm Ail} n_{\rm i}^2 / n(n+p) \tag{2}$$

$$\begin{split} \tau_{Ail} &= 3.8 \times 10^{-18} \epsilon^2 (1+\mu) 1/2 (1+2\mu) / ((m_e/m_o) \\ &|F_1F_2|^2 (kT/E_g)^{3/2}) exp((1+\mu)Eg/(1+\mu)kT) \end{split} \tag{3}$$

where n_i is the intrinsic carrier concentration; n and p are the electron and hole concentrations; N_a is the acceptor concentration; τ_{Ai1} is the intrinsic Auger lifetime for electrons; $\mu = m_e{}^*/m_h{}^*$, the ratio of electron to hole effective masses; E_g is the bandgap; $|F_1F_2|$ is the overlap integral of the interacting electron wave functions; and ϵ is the static dielectric constant. The Auger7 component has been chosen to fit recent unpublished data taken at DRS on extrinsically doped Au- and Cu-doped HgCdTe in the $1-6 \times 10^{16} \, {\rm cm}^{-3}$ range, which indicates that $\tau_{Ai7} \sim 40 \tau_{Ai1}$ for p-doping concentrations $>>10^{16} \, {\rm cm}^{-3}$.

The arsenic-doped material has been used to fabricate HDVIP test diodes by a combination etch/



Fig. 7. Minority carrier lifetimes of Au and arsenic-doped MWIR (5.2 µm at 77 K) and LWIR (10 µm at 77 K) HgCdTe at 77 K.



Fig. 8. The I-V characteristics of an HDVIP, arsenic-doped MWIR (5.2 μm at 77 K) HgCdTe test diode at various temperatures.

implant process, as used in the Group IB doped case. The vacancy concentration was estimated to be ~ 1.4 $imes 10^{15}$ cm $^{-3}$, and the slice was \sim 9- μ m thick. A set of I-V curves as a function of temperature is shown in Fig. 8 for one specific device, which has the same geometry as the diodes in Fig. 4. The idiosyncrasies of the I-V curves are again similar to Fig. 4, except at high temperatures, the de-biasing of the guard diode is much less pronounced. The dark current for the most part is again seen to be diffusion-limited and comparable in value to the Au-doped diode case. Again the dark current at the lowest temperatures is instrumentation-limited, but there is a suggestion of a nondiffusion-like contribution. Also, contrary to expectations, shunting was observed on the smaller pitch diodes with large via diameters. This unexpected phenomenon is depicted in Fig. 9. The etch/implantation process again generates Hg interstitials, which appear to type convert a region of ar-



Fig. 9. Proposed diode-formation process in arsenic-doped HgCdTe.

senic-doped material to n-type, with n $\sim 10^{15}$ cm⁻³, which is approximately equal to the base arsenic concentration, leading to the unexpected shunting and possibly to the nondiffusion-like dark current hinted at low temperatures. The creation of an n-type region in arsenic-doped MWIR HgCdTe has been reported previously.⁶

The type-conversion phenomenon reported here was investigated in separate experiments in which a blanket planar-damaging etch was applied to arsenic-doped MWIR HgCdTe, followed by differential Hall measurements. The type-converted region was indeed observed at a level of $\sim 10^{15}$ cm⁻³. The SIMS measurements of the slice indicated that arsenic was still present in the type-converted volume. The sample was then subjected to varying degrees of annealing in nitrogen, at process-compatible temperatures in the 120–140°C range. The sample converted back to its original p-type characteristics.

The data suggest that when arsenic-doped HgCdTe is subjected to a damaging etch a complex is formed

by the nonequilibrium flux of metal interstitials, possibly with arsenic or even another impurity that is present in appropriate concentrations. This complex is then broken up by the elevated temperature anneal, resulting in a n^+/p^- junction architecture. This thesis is currently under further investigation.

SUMMARY

The HDVIP diodes have been successfully fabricated in 10^{15} cm⁻³, arsenic-doped, MWIR HgCdTe grown from a Te-rich melt. The diode performance was approximately equivalent to diodes fabricated on Au-doped MWIR HgCdTe with similar vacancy concentrations. An unexpected phenomenon was observed in the diode-formation process, which indicated type conversion of arsenic-doped HgCdTe associated with the influx of metal interstitials generated by the etch/implant process. The phenomenon is suggestive of a complex formed by the metal interstitial flux and a residual impurity, possibly arsenic. Annealing at 120–140°C in nitrogen is found to reverse the effect.

The formation of HDVIP n^+/p^- diodes in arsenicdoped HgCdTe offers the potential for high-density focal plane arrays with minimal dark currents.

REFERENCES

- L. Wang, M.H. Yang, M.A. Kinch, P.K. Liao, F. Aqariden, H.F. Schaake, and H.-D. Shih, (Paper presented at the 2003 U.S. Workshop on the Physics and Chemistry of II-VI Materials, New Orleans, LA, 17-19 September 2003).
- D. Chandra, H.F. Schaake, M.A. Kinch, F. Aqariden, C.-F. Wan, D.F. Weirauch, and H.-D. Shih, *J. Electron. Mater.* 31, 715 (2002).
- D. Chandra, D.F. Weirauch, H.F. Schaake, M.A. Kinch, F. Aqariden, C.-F. Wan, H.-D. Shih, (Paper presented at the 2003 U.S. Workshop on the Physics and Chemistry of II-VI Materials, New Orleans, LA, 17-19 September 2003).
- M.C. Chen, L. Colombo, J.A. Dodge, and J.H. Tregilgas, J. Electron. Mater. 24, 539 (1994).
- 5. M.A. Kinch, Proc. SPIE 4369, 566 (2001).
- J.F. Siliquini, J.M. Dell, C.A. Musca, E.P.G. Smith, L. Faraone, and J. Piotrowski, *Appl. Phys. Lett.* 72, 52 (1998).