

Toward a Monolithic Lattice-Matched III-V on Silicon Tandem Solar Cell

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TOWARD A MONOLITHIC LATTICE-MATCHED III-V ON SILICON TANDEM SOLAR CELL

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ABSTRACT: A two-junction device consisting of a 1.7-eV GaNPAs junction on a 1.1-eV silicon junction has the theoretical potential to achieve nearly optimal efficiency for a two-junction tandem cell. We have demonstrated some of the key components toward realizing such a cell, including GaNPAs top cells grown on silicon substrates, GaP-based tunnel junctions grown on silicon substrates, and diffused silicon junctions formed during the epitaxial growth of GaNP on silicon. These components have required the development of techniques for the growth of high crystalline quality GaNPAs on silicon by metal-organic vapor-phase epitaxy.

Keywords: Multijunction Solar Cell, III-V Semiconductors, c-Si

1 INTRODUCTION

III-V semiconductors grown on silicon substrates are very attractive for lower-cost, high-efficiency multijunction solar cells. A two-junction device consisting of a 1.7-eV junction on a 1.1-eV silicon junction has the theoretical potential to achieve nearly optimal efficiency for a two-junction cell [1]. Prior to this work, virtually all of the work on such a structure focused on III-V top cells that were lattice-mismatched to the silicon bottom cell. Under the best conditions, this leads to a threading dislocation density on the order of 10^6 cm^{-2} in the III-V top cell [2]. Under most conditions, this dislocation density decreases the electronic quality of the top cell to the point that a lattice-matched tandem solar cell with a less optimal band-gap combination (e.g. GaInP/GaAs) is much more efficient [3,4].

$\text{GaN}_x\text{P}_{1-x-y}\text{As}_y$, hereafter GaNPAs, is a direct-gap [5] III-V alloy that can be grown lattice-matched to Si with very low structural defect densities [6]. We have proposed the use of lattice-matched GaNPAs on silicon for high-efficiency multijunction solar cells [7]. Such a

cell would have application in space power systems, as well as terrestrial concentrators. In this paper, we present the progress of our efforts toward realizing such a cell.

2 GROWTH OF GaNP(As) ON SILICON

Epitaxial $\text{GaN}_x\text{P}_{1-x-y}\text{As}_y$ and $\text{GaN}_x\text{P}_{1-x}$ layers were grown on single-crystal Czochralski silicon substrates by atmospheric-pressure metal-organic chemical vapor phase epitaxy (MOVPE) using triethylgallium, phosphine (PH_3), t-butylarsine (TBA), and dimethylhydrazine (DMH) sources. Prior to growth, the silicon substrates were cleaned in an ammonia/peroxide solution, rinsed in deionized water, and spun dry. The native silicon oxide was removed *in situ* by annealing at 1000°C under H_2 . A thin ($<40 \text{ nm}$) GaP nucleation layer was grown under a high partial pressure of PH_3 ($\sim 10 \text{ torr}$) while reducing the temperature to 800°C at $100^\circ\text{C}/\text{min}$. A $0.5 \mu\text{m}$ thick $\text{GaN}_{0.02}\text{P}_{0.98}$ buffer layer was then grown at 700°C at $1 \mu\text{m}/\text{h}$.

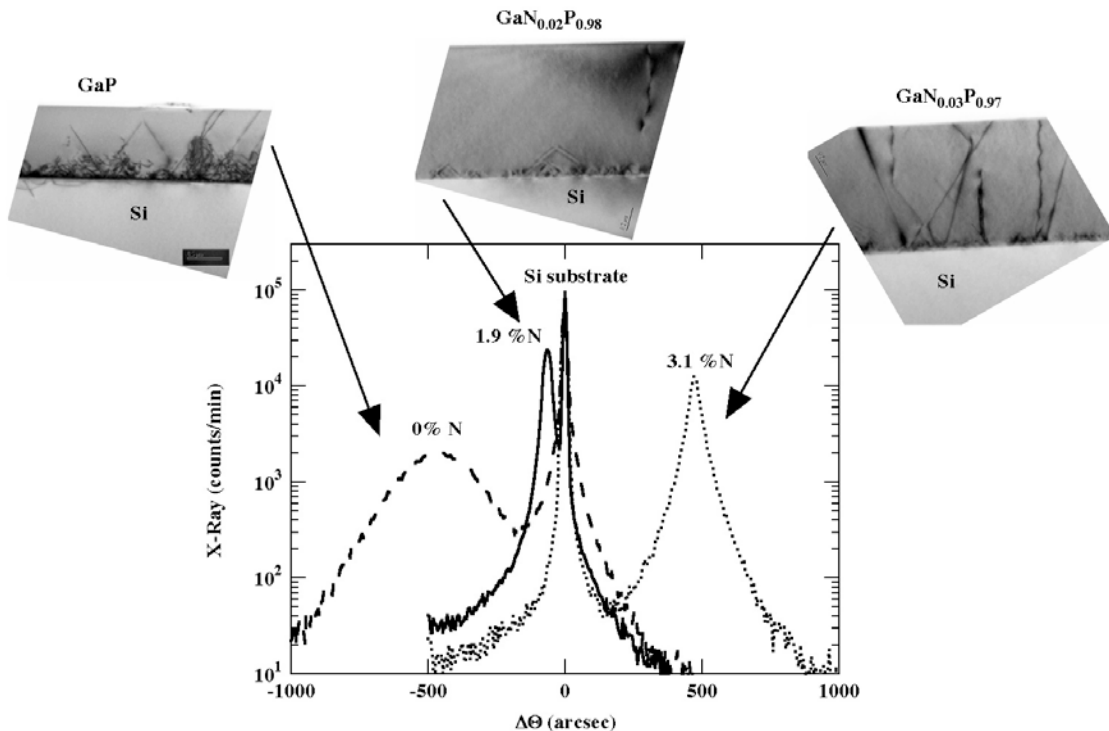


Figure 1: X-ray diffraction of $\text{GaN}_x\text{P}_{1-x}$ grown on silicon taken in (004) reflection with corresponding TEM images.

Using this nucleation scheme [8], high crystalline quality was achieved only when the thicker GaNP layer was closely lattice-matched to the silicon. Figure 1 shows transmission electron microscope (TEM) images and X-ray diffraction results of various compositions of GaNP layers. The lattice-matched $\text{GaN}_{0.02}\text{P}_{0.98}$ layer shows low defect density away from the interface and X-ray peak widths as low as 24 arcsec. In spite of an imperfect nucleation scheme, the defects apparent at the GaP/Si interface appear not to propagate into the epilayer during the growth of the lattice-matched composition.

By varying the lattice-matched composition of $\text{GaN}_x\text{P}_{1-x-y}\text{As}_y$, direct bandgaps in the range of 1.5 to 2.0 eV were achieved [7]. Figure 2 shows the optical absorption coefficient of a series of GaNPAs layers grown lattice-matched on GaP substrates.

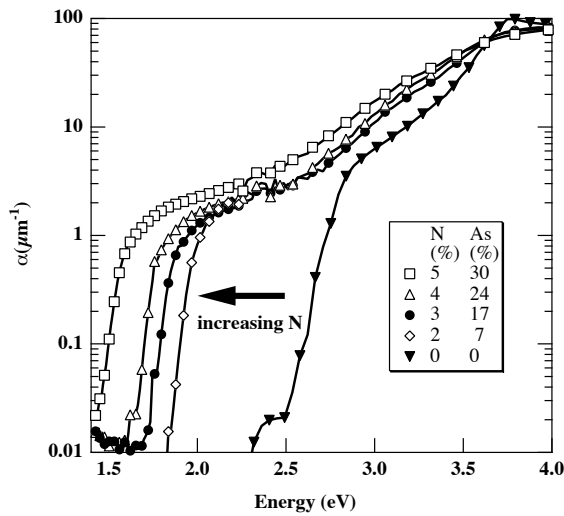


Figure 2: Absorption coefficient of GaP and GaNPAs layers grown on GaP substrates as determined from transmission and spectral ellipsometry data.

The electrical quality of GaNP(As) has been shown to be highly dependent on growth conditions. In particular, growth conditions that minimize unintentional carbon and hydrogen contamination provide the highest carrier lifetimes [9]. These conditions were used for optimal performance of the GaNPAs top cells.

3 SILICON BOTTOM CELL

During the epitaxial growth of GaNPAs on silicon at 700°C , significant diffusion of the III-V atoms into the silicon occurs. When a $0.5\text{-}\mu\text{m}$ $\text{GaN}_{0.02}\text{P}_{0.98}$ layer is grown on a p-type, B-doped silicon ($1\text{-}10\ \Omega\text{-cm}$) substrate, an n-p homojunction is created in the silicon. But when the same layer is grown on an n-type, P-doped silicon ($1\text{-}10\ \Omega\text{-cm}$) substrate, no silicon homojunction is created. This is because a greater concentration of P than Ga diffuses into the silicon from the III-V epilayers. By selectively etching the III-V from the silicon using a $3\ \text{HCl} : 1\ \text{HNO}_3$ solution, we were able to analyze the diffused junction formed in the p-type silicon during growth of the GaNP layer. Figure 3 shows the P concentration profile as measured by secondary ion-mass spectroscopy (SIMS), as well as the donor concentration profile as measured by electrochemical capacitance-voltage (CV) measurements. From these data, we deduce that the thickness of the diffused emitter in this cell is

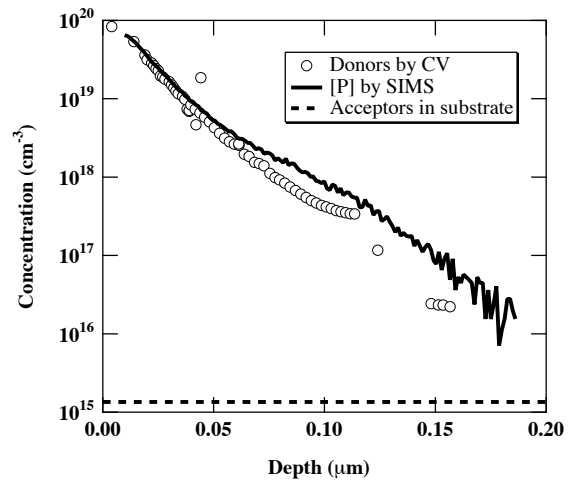


Figure 3: Profile of donors and phosphorous atoms diffused into silicon substrate during GaNP growth.

approximately $2000\ \text{\AA}$. This thickness will vary with time and temperature of the III-V growth.

We have fabricated a functioning silicon cell from this diffused silicon homojunction. The front side was contacted with a gold grid on a thin Se-doped GaAs contact layer grown on the $0.5\text{-}\mu\text{m}$ Se-doped $\text{GaN}_{0.02}\text{P}_{0.98}$ layer. An annealed aluminum back-contact formed a back-surface field. For some devices, the aluminum was evaporated on the back after III-V growth, then annealed 5 minutes at 700°C under H_2 . For other devices, an Al/Mo bilayer was evaporated onto the back before III-V growth. The back-surface field was then formed during the high-temperature III-V growth. This technique eliminated the need for an extra annealing step and helps reduce post-growth diffusion in the structure. Figure 4 shows the internal quantum efficiency (QE) and current-voltage (IV) characteristics of this silicon cell. The cell containing only a $0.5\text{-}\mu\text{m}$ GaNP buffer has an internal quantum efficiency of 90% below the band edge of the GaNP, a fill factor of 71%, and V_{oc} of 549 mV. The relatively thick emitter and defects at the III-V/Si interface (see Fig. 1) are likely to result in poor blue response of this junction; but this is not a major concern, because in the full tandem structure, the high energy light

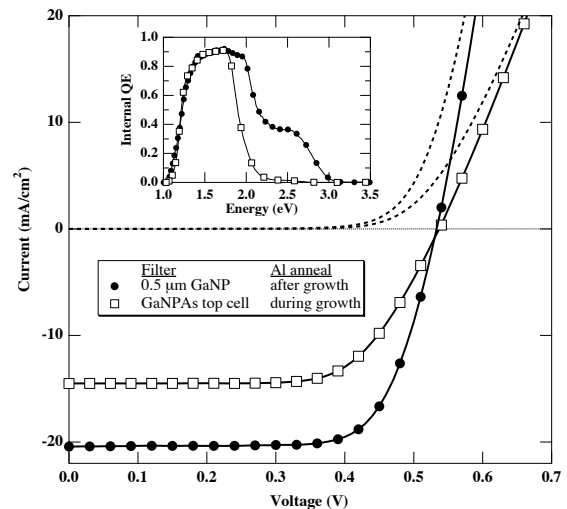


Figure 4: Light and dark (dashed) IV curves of Si homojunction cells formed during III-V growth. The inset graph shows internal QE of the same cells.

will be collected in a GaNPAs top cell, rather than the silicon cell. Here, the high-energy light is just filtered by the GaNP layers above the junction. The other Si cell shown contains a filter simulating a 1.8-eV GaNPAs cell. This GaNPAs filter is identical to the cells discussed in section 5 (see Fig. 7), but is doped entirely n-type. This Si device has an AM1.5G J_{sc} of 15 mA/cm^2 .

The red responses of these silicon cells are quite satisfactory for our purposes at this point. This can be improved in the future, if necessary, by using higher quality float-zone silicon substrates or optimizing the back-surface field.

4 TUNNEL JUNCTION

If the n-on-p silicon homojunction described above is to be used in a tandem cell, a p+-on-n+ highly conductive tunnel junction must be developed. This will require extremely high doping levels in GaP or GaNP materials near a sharp interface. Se doping in GaNP is very efficient and high electron concentrations can be achieved, similar to Se doping of GaNAs [10]. P-type doping using Zn or C [9] in GaNP is not as well understood. Zn is a common dopant in GaP but requires low temperatures for high incorporation. Unfortunately, both Se and Zn dopants tend to diffuse quite readily.

Using an n-type silicon substrate, we are able to study tunnel junctions grown on silicon without forming a silicon junction. A Zn-doped GaP on Se-doped GaNP structure resulted in a fairly low-resistance ($0.14 \Omega \text{ cm}^2$) ohmic tunnel junction, but in this case, an annealed Pd/Zn/Pd contact was deposited directly onto the GaP:Zn. The diffusion of Zn from the metal contact most likely improved the tunnel junction, because an identical tunnel junction using unannealed Au / GaAs:Zn contacts was non-ohmic. The same tunnel junction was used in cells described in the following sections, but they did not function properly. Clearly, increased p-type doping is needed to form a functioning tunnel junction in a tandem structure.

5 GaNPAs TOP CELL

GaNPAs top cells were grown on GaP [7] and silicon substrates as discussed earlier. Ti/Pd/Al/Pd/Au was used as a back-contact to the n-type silicon substrates. Annealed Pd/Zn/Pd was used to contact the p-type GaP substrates. Gold grids were deposited onto a thin (70 nm) highly doped GaAs contacting layer on the front of the cell. The GaAs contact layer was then selectively etched from between the grid fingers.

Similar to the case of most GaInNAs material [11], GaNPAs grown to-date appears to have very short diffusion lengths, even when special care is taken to minimize H and C contamination. Figure 5 shows how the spectral response of $\text{GaN}_{0.02}\text{P}_{0.98}$ grown on silicon increases dramatically with the depletion width. Thus, p-i-n or n-i-p devices employing field-aided collection are used to maximize QE. Unlike the GaInNAs material, the GaNPAs can be easily grown with very low carrier concentrations to achieve thick intrinsic layers in these devices, and thus, high QEs.

Because GaNP growth on p-type silicon always seems to result in a diffused homojunction, we must include a tunnel junction to study a single-junction n-i-p GaNPAs top cell grown on silicon. This is the same structure as the tandem shown in Fig. 7 except the silicon

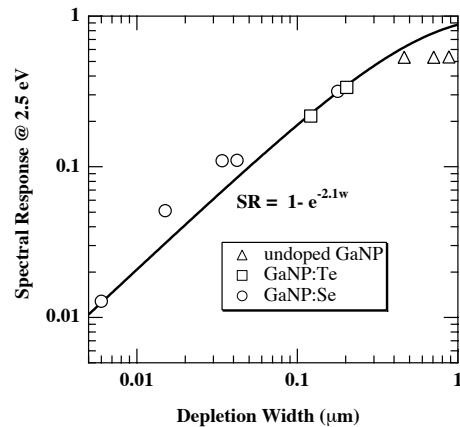


Figure 5: Spectral response of $\text{GaN}_{0.02}\text{P}_{0.98}$ grown on silicon for a variety of n-type doping levels. The fit implies $\alpha \sim 2.1 \mu\text{m}^{-1}$ consistent with Fig. 2.

is n-type. We have previously studied n-i-p GaNPAs cells grown on p-type GaP [7], but these are grown to a slightly different composition to lattice-match to GaP, rather than silicon. We have also fabricated p-i-n GaNPAs cells on n-type silicon. Characteristic results of these different types of GaNPAs are shown in Fig. 6.

P-i-n $\text{GaN}_{0.02}\text{P}_{0.98}$ cells grown on silicon with a band gap of 1.98 eV have achieved internal quantum efficiencies of 60%, fill factors of 60%, and V_{oc} of 1.2 V. The n-i-p GaNPAs cells grown on GaP with a band gap of 1.82 eV have also achieved internal QEs of 60% and fill factors of 60%, but lower V_{oc} of 1.0 V due to the lower band gap. Both of these V_{oc} s relative to their band gaps are lower than we would expect for high-quality solar cell materials. The n-i-p GaNPAs cells grown on silicon gave similar QE results, but an apparent bucking junction from an inadequate tunnel junction results in a lower fill factor and increased series resistance. The tunnel junction used here was the same as the successful tunnel junction discussed in section 4, but without the Zn diffused from the metal contact.

The largest AM1.5G J_{sc} that we have achieved in a III-V top cell on Si is about 6.4 mA/cm^2 using 1.8-eV GaNPAs. To current match this top cell to the bottom Si

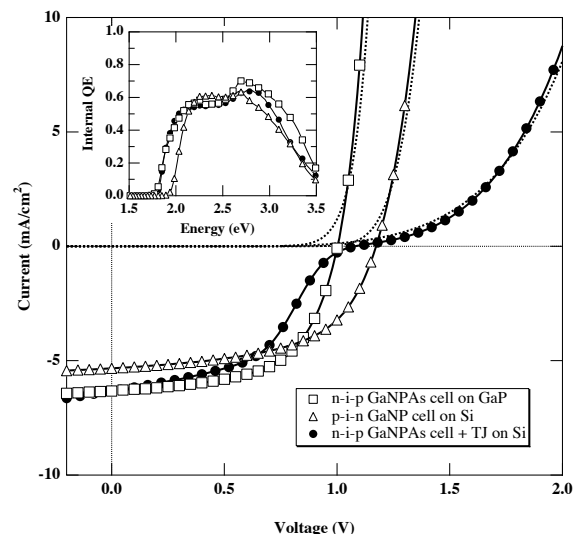


Figure 6: IV curves of single-junction GaNP(As) cells. The inset graph shows the internal QE of the same cells.

cell, we need to increase the QE and/or reduce the band gap. Reducing the band gap by increasing nitrogen and arsenic concentration tends to result in lower-quality material and also reduces the J_{sc} of the bottom cell. If a field-aided device is used, increasing the thickness while reducing the carrier concentration in the intrinsic layer may help increase the QE.

Increasing the diffusion length in these materials is the preferable method of increasing the QE. Growth conditions may be further optimized to reduce unintentional carbon and/or hydrogen impurities. Improved nucleation of GaP on silicon may also help by reducing the defect densities that are currently on the order of 10^7 cm^{-2} , as observed by electron-beam-induced current (EBIC) images.

Another problem with the current GaNPAs top cells is an extremely high emitter sheet resistance. The GaNP(As) emitter materials grown so far have very low mobility and must be highly doped to achieve a sheet resistance of even $10 \text{ k}\Omega/\text{sq}$. This loss mechanism becomes even more pronounced under concentration.

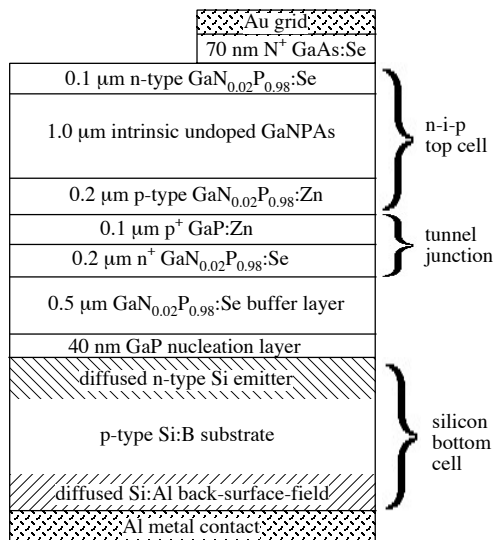


Figure 7: Schematic of full tandem structure.

6 TANDEM

We put these components together into the tandem device shown in Fig. 7. Figure 8 shows the performance of this tandem cell, along with the performance of single-junction cells grown in nearly identical structures. This tandem cell is not well current-matched; the top GaNPAs junction limits the current. As discussed above, this top-cell current must be increased. It is clear that the tandem cell has a voltage boost over the single-junction top cell. The poor tunnel junction affects the tandem cell in the same way that it affects the single-junction top cell.

7 CONCLUSION

We have demonstrated the first lattice-matched III-V on silicon tandem solar cell. For such a tandem solar cell to achieve efficiencies greater than current state-of-the-art silicon cells and compete with GaInP/GaAs/Ge solar cells, the performance of the top GaNPAs junction and tunnel junction must be further improved. These

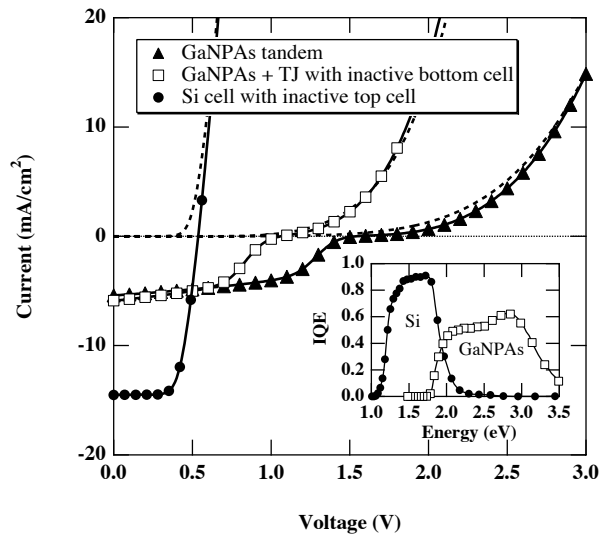


Figure 8: Light and dark (dashed) IV curves of tandem and single-junction cells. The inset shows internal QE.

improvements will require better control over nucleation of III-V on silicon substrates, doping of GaP and GaNP(As) materials, and material quality of GaNP(As).

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REFERENCES

- [1] S. R. Kurtz, P. Faine, J. M. Olson, *J. Appl. Phys.* 68 (1990) 1890.
- [2] T. Soga, H. Nishikawa, T. Jimbo, M. Umeno, *J. Cryst. Growth* 107 (1991) 479.
- [3] J. M. Olson, T. Gessert, M. M. Al-Jassim, *Proceedings 18th IEEE Photovoltaic Specialists Conference*, (1985) 552.
- [4] J. M. Olson, S. R. Kurtz, A. E. Kibbler, P. Faine, *Appl. Phys. Lett.* 56 (1990) 623.
- [5] H. P. Xin, C. W. Tu, Y. Zhang, A. Mascarenhas, *Appl. Phys. Lett.* 76 (2000) 1267.
- [6] H. Yonezu, *Semicond. Sci. Tech.* 17 (2002) 762.
- [7] J. Geisz, D. J. Friedman, S. Kurtz, *Proceedings 29th IEEE Photovoltaic Specialists Conference*, New Orleans, (2002) 864.
- [8] J. F. Geisz, J. M. Olson, W. E. McMahon, T. Hannappel, *et al.*, *Proceedings Material Research Society*, Boston, MA, Vol. 799 (2003) 27.
- [9] J. F. Geisz, R. C. Reedy, B. M. Keyes, W. K. Metzger, *J. Cryst. Growth* 259 (2003) 223.
- [10] K. M. Yu, W. Walukiewicz, W. Shan, J. W. Ager, J. Wu, E. E. Haller, J. F. Geisz, D. J. Friedman, J. M. Olson, *Phys. Rev. B* 61 (2000) R13337.
- [11] J. F. Geisz, D. J. Friedman, J. M. Olson, S. R. Kurtz, B. M. Keyes, *J. Cryst. Growth* 195 (1998) 401.

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