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Sb/GaSb Multilayer Structures for Potential Application as an Indirect Narrow Bandgap Material

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We provide rational, and experimental results of an exploratory investigation into the Sb/GaSb system as a potential indirect narrow-gap superlattice, where spacial quantization effects are proposed to induce a positive valence-conduction band energy gap in the Sb semimetal layers. The experimental study has investigated growth of Sb/GaSb single heterojunctions and elementary multilayer structures using molecular beam epitaxy. Electrical properties of Sb epilayers with thicknesses in the range 150-2500Å have been determined by temperature dependent Hall.

I. INTRODUCTION

Metal-semiconductor and semimetal-semiconductor layered structures are currently of significant interest due to the novel devices and physics that can be conceived when the transport properties of semiconductors and (semi)metals are combined.

While the motivation for including metals in semiconductor heterostructures has primarily been their low resistivity, permitting fabrication of buried contacts, interconnects, and ground planes which are considered essential to the three-dimensional integration of semiconductor devices, we point out[1] that semimetals can also provide similar conductivities, and in addition the further possibility of unique transport, optical and nonlinear properties brought about by quantum size effects.

The quantum size effect is generally defined as a dependence of the thermodynamic properties and kinetic coefficients of a solid on its characteristic geometric dimensions, when the latter becomes comparable to the de Broglie wavelength of the charge carriers. When the film thickness is much less than the two in-plane dimensions ($L_z << L_x, L_y$), and is comparable to the de Broglie wavelength of the carriers, quantization of the carrier motion in the z direction occurs.

The group V semimetals (Sb and Bi) provide an excellent system for the study of quantum size effects. For these materials the conduction band minimum (3-fold degenerate at the L-point) lies at a lower energy than the valence band maximum (6-fold at the H-point in Sb, 1-fold at the T-point in Bi). The overlap of the two bands is ≈ 180 meV in Sb and ≈ 40 meV in Bi (see Fig: 1a).

Both Sb and Bi have large characteristic lengths: the mean free path is a few microns and the de Broglie wavelength ≈ 400Å. Consequently, interesting transport phenomena are expected if the carriers in these semimetals are spacially confined. Such confinement can be achieved by sandwiching the semimetal film between layers of a suitable barrier material. That material should posses a sufficiently wide energy gap to provide acceptably large conduction and valence band offsets to the semimetal charge carriers, but must also be compatible with the semimetal in terms of growth, chemistry, and crystalographic structure. While previous studies investigated the CdTe-Bi system[2] optimal heterostructure properties were not achieved.

In this paper we outline the rational from the materials and electronic perspective for the investigation of the Sb/GaSb material system and provide some experimental results for the growth and electronic properties of Sb/GaSb epilayers.

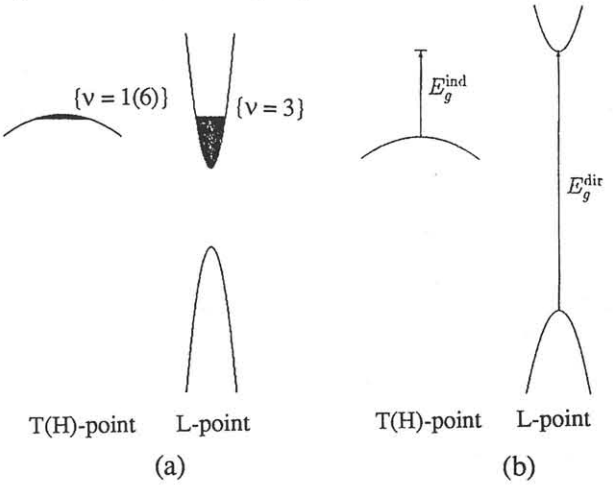

Fig: 1. Schematic of E-k relation for Bi(Sb) in bulk (a), and in quantum well (b).

The bulk structure of Sb is rhombohedral (trigonal) with a lattice parameter a = 4.5064Å and α = 57.11°[3], while GaSb is zincblende with a = 6.0959Å.

However, the (111) plane of Sb forms a hexagonal surface net, and is structurally very similar to that of zincblende normal to the <111> direction. One obtains a (111) planar mismatch, $\Delta a_i/a_i$, between Sb and GaSb of only 0.0006 (at 273K). We also note that the coefficents of linear expansion for Sb and GaSb are comparable ($\alpha_{GaSb} = 6.9 \times 10^{-6}$, $\alpha_{Sb} = 9 \times 10^{-6}$) and because Sb is common in the Sb/GaSb system cross doping concerns experienced in the other semimetal/semiconductor combinations investigated are eliminated.

Based on a consideration of quantum confinement effects on the energy bands in elemental Sb, we expect Sb-GaSb superlattices to have several unique properties which may be highly attractive for optical devices operating in the infrared (IR). For example, while conventional narrow-gap semiconductors display large optical nonlinearities associated with free-carrier plasma generation the performance of these materials in devices is severely limited by saturation of the nonlinearities at high optical intensities.[4] It has recently been pointed out[5] that the saturation properties may be substantially improved by employing a semiconductor with a narrow, indirect energy gap. In a quantum well or superlattice such as shown in Fig: 1(b) the conduction band should move up in energy while the valence band moves down. At some point, the two will cross and we enter the indirect narrow-gap semiconductor (INGS) regime, which is unique among naturally-occurring and man-made semiconductors[6]. As in germanium and silicon, which have much wider indirect gaps, one then expects the Auger recombination lifetime to be orders of magnitude longer than those observed in direct-gap semiconductors with the same E_g (due to the difficulty of conserving both momentum and energy). Also significant is that the absorption coefficient for optical transitions across the indirect gap will be far smaller than that for the direct transitions in bulk $Bi_{1-x}Sb_x$. This favorable combination of properties could lead to a new generation of all-optical switching devices operating in the infrared.

II. EXPERIMENTAL

The films were grown by molecular beam epitaxy (MBE) in a commercial (Riber 32) growth chamber, using a standard Sb effusion cell producing Sb_4, and a standard liquid-metal Ga source. The substrates employed were nominally undoped (p-type) GaSb(100), (111)A and (111)B, indium-bonded to Molybdenum blocks. Molecular fluxes were determined from measurements by an ion gauge interposed in the beam path. Substrate temperatures above 425°C were measured by an optical pyrometer, and below 425°C were estimated by extrapolating readings from a thermocouple mounted behind the sample block. Growth rates for the GaSb and Sb were calibrated by Rutherford backscattering spectrometry. Growth was monitored by *in-situ* reflection high energy electron diffraction (RHEED). Electrical measurements were conducted using a standard Hall system taken over a temperature range 4 - 300K. Contacts were made using an In-Sn alloy, annealed at 220°C, in a Van der Pauw geometry.

III. RESULTS AND DISCUSSION

Growth of Sb on GaSb for the (100), (111)A and (111)B orientations was investigated. Details of our investigation into the MBE growth of GaSb on (111)A and (111)B orientations are reported elsewhere[7]. All attempts to grow Sb epitaxially on GaSb(100) failed, most likely due to the unfavorable registry between the square surface net of GaSb(100) and the naturally forming hexagonal (111) plane of Sb. However, epitaxial growth of Sb on both GaSb (111)A and (111)B was successful and was achieved by increasing the Sb residence lifetime on the GaSb surface by lowering the temperature below a nucleation temperature, $T_n(J_{Sb})$, which we found to be independent of the growth orientation. For J_{Sb} employed in our study, $T_n = 260°C$. For epitaxy on both (111)A and (111)B we found that initial growth was slow and simultaneous diffraction from epitaxial Sb and GaSb was observed by RHEED. A streaked, well defined (1x1) RHEED pattern, showing single phase, two dimensional growth resulted after surface coverage was complete. Epitaxial growth, once established, could be continued to approximately 200°C. Below this temperature, diffraction rings indicative of polycrystalline growth were observed.

Our studies found that with Sb flux constantly present on the GaSb surface, the slow initial growth, where surface accommodation and desorption were only slightly unbalanced, was a most critical condition for epitaxy. For example, if the surface concentration of Sb was increased rapidly by cooling quickly through T_n, multiply oriented, three-dimensional growth occured. However, we found that Sb could be successfully nucleated below T_n if the GaSb surface was not exposed to a Sb flux for a period of several seconds. Such results suggest that the successful nucleation of Sb is quite sensitive to the degree of Sb surface coverage on the GaSb surface.

The ability to nucleate and grow epitaxial Sb permitted us to investigate the growth of GaSb on the Sb epilayers. Upon initiation of GaSb growth the streaked (1x1) Sb RHEED pattern evolved into a pattern of 1x1 wide streaks with broad spots, indicative of a surface which is rough on the order of a few monolayers. This pattern remained throughout growth of GaSb. XPS extinction curves were obtained, and indicated a two dimensional growth mode. The RHEED and XPS studies suggest that the GaSb growth is rough over the order of several monolayers, and x-ray studies are currently underway to characterize these films.

Hall data for the temperature range 5-300K were taken on a series of single Sb epilayer films grown on GaSb(111)A. Results for films having nominal thicknesses spanning the range 160Å - 2500Å are summarized in Table I.

Sb thick-ness (Å)	Mobility ($\mu_n + \mu_p$) ($cm^2/V\text{-}s$)		Resistivity (μ Ohm -cm)		Hall Coefficient ($cm3\ C^{-1}$) ($x10^4$)	
	77K	5K	77K	5K	77K	5K
2500	5083	5222	0.22	0.10	-11	-6.5
750	1065	185	3.87	1.81	41	3.4
375	489	271	1.75	4.22	8.5	9.2
160	1044	37	2.25	5.81	24	2.2

TABLE I

The decrease in mobility as layer thickness is decreased suggests that an interface/surface scattering process dominates. Such a mechanism is also supported by the resistance-vs-temperature data which are shown in Fig. 2. Although this sample exhibits metallic behavior, (all samples exhibited similar temperature dependence) the variation of resistivity throughout the temperature range is small compared to that of bulk Sb ($\rho(300K)/\rho(4K) = 10^3$, implying that scattering at the surface and/or interface (which is a temperature independent mechanism) plays an important role.

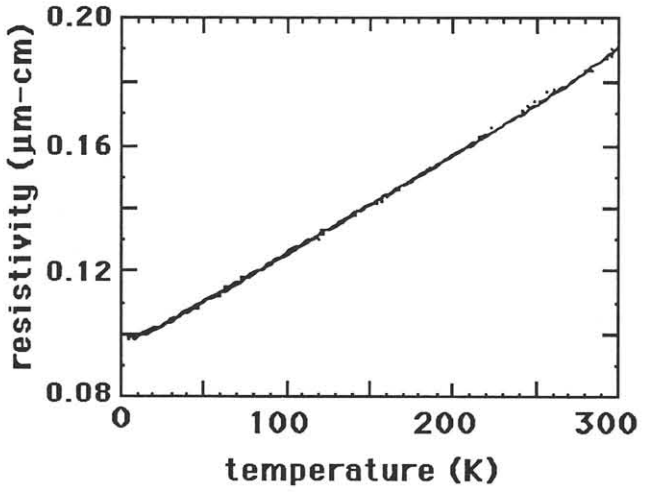

Fig.2 Resistivity-vs-temperature for nominal 2500Å-thick Sb epilayer.

The change from a negative to positive Hall coefficient as layer thickness is decreased is of interest. For a parabolic two band system, with both electrons and holes as charged carriers the Hall coefficient has the form

$$R_H = \frac{p\mu_p^2 - n\mu_n^2}{e\,(p\mu_p + n\,\mu_n)}$$

where μ_n and μ_p are the mobilities, and n and p the carrier concentrations, of electrons and holes respectively. In a bulk semimetal $n \approx p$, and in bulk Sb, $R_H < 0$, which implies $\mu_n > \mu_p$. However, the samples investigated become p-type ($R_H > 0$) as the layer thickness L_z of the Sb was decreased, which we propose to be either due to strong surface scattering, for which μ_n may become smaller than μp, or due to electron transfer between the Sb and GaSb.

IV. CONCLUSIONS

The Sb/GaSb system has been proposed as a potential indirect narrow bandgap material. The initial experimental investigation has shown that Sb/GaSb single heterojunctions and multilayer structures can be grown. Hall studies of Sb epilayers suggest that the transport may be dominated by scattering at the surface and/or interface, and a change from n to p-type is observed as the sample thickness is decreased from 2500Å to 750Å, which we tentatively explain as due to either a strong surface scattering mechanism or due to size quantization effects. Future studies are underway to characterize transport and optical properties of Sb/GaSb multilayer structures.

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6 Strictly speaking, $Bi_{1-x}Sb_x$ becomes a semiconductor at $x > 0.08$ [V. G. Alekseyeva, T. M. Lifshits, Ye. G. Chirkova, and A. Ya. Shul'man, *Radio Engr. Electron. Phys.* **23**, No. 9, 124 (1978)]. However, the indirect energy gap never exceeds 20 meV, which is too small compared to typical thermal energies to be useful in the applications envisioned here.

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