Synthesis of Superhard Thin Films and Coatings Based on Light Elements

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13. ABSTRACT (Maximum 200 words)
Superhard, dielectric, and optoelectronic materials in the Si-C-N-N, Si-B-O-N and Zr-Bi-Si-N systems were prepared as thin films via novel CVD and MBE methods. SiC and AlN, normally insoluble in each other below 2000°C are combined to form single phase SiAlN by gas source MBE of SiH4:CN and Al atoms at 750°C. The growth of optoelectrical materials takes place on SiC and Si(111) Commensurate heterolayer between Si(111) and SiAlN is facilitated by the presence of a crystalline (Si-O-Al=Si) oxide at the Si interface. The bandgap of SiAlN is 3.2 eV and average hardness is 25 GPa. Superhard metal borides such as ZrB2 and ternary analogs have been grown as perfectly epitaxial layers on Si(111). These materials in turn are used as totally reflective and lattice-matched buffer layers for integration of light emitting nitrides (GaN and AlGaN) with Si. UV-CVD growth of single-phase Ge1-xSb1-xSe semiconductors is conducted for the first time on Si(100). These materials exhibit tunable band gaps and possess lattice constants above and below that of Ge. The fabrication of Ge1-xSb1-xSe makes it possible to decouple strain and band gap engineering to achieve unique-structures that lead to novel photonic devices based entirely on group IV materials (covering a wide range of operating wavelengths in the IR). Growth of random Ge0.9Sb0.1 alloys and related ordered structures has been achieved directly on Si(100). Optical characteristics show a Ge-like band structure. The band gaps and critical point energies are reduced monotonically with Sn content indicating that band gap engineering has been obtained in this system.

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4. Darrick Williams, B. Pleune, C. Leinenweber, and J. Kouvetakis “Synthesis and structural properties of stoichiometric framework C-N compounds of Be, Mg, Al, and Ti”, \textit{J. of Solid State Chem.} 159, 244-250 (2001).


**Patents Arising from ARO Support**


**Completed Ph.D. and MS Dissertations**

1. Jennifer Taraci, Ph.D Chemistry, December 2002, “New semiconductor heterostructures and nanostructures in the C-Si-Ge-Sn system”.


5. Levi Torrison Ph.D. Chemistry Fall 2003. “Si-based nanostructures and dielectrics”.

6. Candi Cook MS, Fall 2003 [Science and Engineering of Materials, (SEM)] “Optical characterization of group IV heterostructures based on silicon germanium and tin”
Summary of Most Important Results

**Si-Ge-Sn alloys grown on Si(100)**

Silicon is the most desirable substrate for the growth of semiconductor materials. Virtually defect-free Si wafers are available at low cost, and the range of applications of any semiconductor grown on Si can be enhanced by integration with silicon-based microelectronics. Unfortunately, the growth of semiconductors on Si is fraught with difficulties. A high quality interface between Si and a direct-gap semiconductor, the key component of any device that integrates optoelectronics with microelectronics, has yet to be demonstrated. Excellent quality Si$_{1-x}$Ge$_x$ alloys can be grown on Si, but the large lattice mismatch between Ge and Si limits considerably the range of Ge-concentrations that can be used.

In this report we describe fabrication and optical properties of device-quality, strain-free Sn$_x$Ge$_{1-x}$ layers grown directly on Si wafers. This is an important development for several reasons. First, Sn$_x$Ge$_{1-x}$ alloys have been predicted to undergo a transition from indirect- to direct-gap semiconductors so that this material may lead to the first direct-gap semiconductor fully integrated with Si technology. Second, device-quality Sn$_x$Ge$_{1-x}$ layers of arbitrary thickness can be deposited on Si, and these can be used as "virtual substrates" for the growth of Sn$_x$Ge$_{1-x}$ alloys of different composition as well as Ge$_{1-x-y}$Si$_x$Sn$_y$ ternary analogs. The fabrication of Ge$_{1-x-y}$Si$_x$Sn$_y$ makes it possible to decouple strain and band gap engineering to achieve unique devices structures that lead to novel photonic devices based entirely on group IV materials. These systems cover a wide range of operating wavelengths in the IR and include strain-engineered direct gap heterodiodes and multi-quantum well lasers, photodetectors, emitters and modulators grown on Sn$_{1-x}$Ge$_x$ and Ge$_{1-x-y}$Si$_x$Sn$_y$ buffered Si.

The **Ge-Sn system** The Sn$_x$Ge$_{1-x}$ alloys are grown by a specially developed UHV-CVD method, which is based on reactions between SnD$_4$ and Ge$_2$H$_6$ (digermane). Depositions were conducted in a custom-built ultra-high- vacuum CVD reactor on Si(001) wafers. Growth temperatures between 250$^\circ$ and 350$^\circ$ produced thick films (50-500 nm) with Sn continuous concentrations up to 20 %, as measured by Rutherford backscattering (RBS). Fig 1 (top panels) shows a comparison between random and aligned RBS spectra for a Sn$_{0.02}$Ge$_{0.98}$ sample and a Sn$_{0.14}$Ge$_{0.86}$ sample. The ratio $\chi_{\text{min}}$ between the aligned and random peak heights is 4% in the $x=0.02$ sample and about 50% in the $x=0.14$ sample for both Ge and Sn. This provides unequivocal proof that Sn occupies substitutional sites in the average diamond structure. The $\chi_{\text{min}}=4\%$ value closely approaches the practical limit of about 3% for structurally perfect Si, which is unprecedented for a binary crystal grown directly on Si. The structural properties of the films were further investigated by XTEM. Electron micrographs demonstrating nearly defect-free growth of Sn$_{0.02}$Ge$_{0.98}$ are shown in the bottom panels of Fig. 1. The images show that the predominant defects accommodating the large misfit between the alloys and the Si substrate are Lomer edge dislocations at the interface. These are parallel to the interface plane and do not degrade the film quality. The surfaces are very smooth,, and atomically flat. Electron and X-ray diffraction experiments show a monotonically increasing average lattice constant as a function of the Sn-concentration, with no evidence for a significant tetragonal distortion.
The optical properties were investigated with infrared spectroscopic ellipsometry. Figure 2 displays the second derivative with respect to energy of the imaginary part of the dielectric function showing that the direct band gap (E_0) for samples containing 2 at % and 14 at % Sn are 0.72 eV to 0.41 eV respectively compared with 0.81 eV for pure Ge. The direct bandgap E_0 is essentially reduced to half of its value in pure Ge for only 14% of Sn in the films. The dramatic reduction in bandgap value indicates that a transition from an indirect to direct bandgap has been achieved.

In conclusion, we have demonstrated a wide tunability of the band structure in SnGe alloys grown on Si. Since our materials grow essentially strain-free, there is in principle no upper limit to the Sn concentration that can be achieved. Thus our approach represents the most straightforward route to direct-gap SnGe alloys and a practical solution to the long-standing problem of growing direct-gap semiconductors on Si. The very large lattice mismatch between our films and the Si substrate opens up intriguing new opportunities for band gap and strain engineering on silicon.

The Si-Ge-Sn system: Very recently we have demonstrated growth of device-quality Si-Ge-Sn ternary materials that possess a variable and controllable range of compositions and exhibit lattice constants above and below that of bulk Ge. These materials form more readily and exhibit greater thermal stability than their Sn-Ge counterparts. Combined with the previous demonstration of Sn_xGe_{1-x} films, the new ternary system provides unprecedented flexibility for band gap and strain engineering in group IV alloys. Possible applications aside from those photonic devices highlighted in the previous sections, include buffer layers for growth of relaxed SiGe alloys with high Ge content and barrier layers for novel type I direct gap Ge quantum wells. We are currently pursuing a vigorous research program in this area to determine the fundamental properties of these materials and to explore practical applications.

The ternaries Ge_{1-x-y}Sn_xSi_y are grown on Si(100) via Ge_{1-x}Sn_x alloy buffer layers as illustrated by the RBS and TEM data in Figure 3. The crystal structure, elemental distribution and morphological properties of the heterostructures are characterized by high-resolution TEM, including electron energy loss nanospectroscopy, x-ray diffraction and AFM. These techniques demonstrate growth of perfectly epitaxial, uniform and highly aligned layers with atomically smooth surfaces and monocristalline structures that have lattice constants close to that of Ge. RBS ion channeling shows that the constituent elements occupy random substitutional sites in the same average diamond cubic lattice and the Raman shifts are consistent with the lattice expansion produced by the Sn incorporation into SiGe tetrahedral sites.

The structural and strain properties of these
materials are still virtually unknown and a multidisciplinary effort to determine these is in currently progress. The lattice constant as a function of composition (especially deviations from linearity) and their strain when grown on Si are investigated by high resolution XRD. Figure 4 shows the x-ray reciprocal space map data of a Si$_{0.20}$Sn$_{0.10}$Ge$_{0.70}$/Sn$_{0.02}$Ge$_{0.98}$/Si(100) heterostructure. The data indicate a fully strained SiGeSn epilayer with respect to the relaxed GeSn buffer layer. Related studies show that tensile strained as well as relaxed SiGeSn films can be obtained on strain-free GeSn buffer layers. These results are exciting because they show for the first time that strain engineering can be achieved in SiGeSn heterostructures and multilayers by tuning the lattice parameter of the GeSn buffer layer. A host of novel strained engineered optical and electronic devices have been designed based on this concept. It is interesting to note that the strain is reliably robust up to at least 400-500°C (400°C is the growth temperature of the films).

We have assembled various combinations of concentrations in the Si-Ge-Sn alloy system to form strained-layer heterostructures, such as Ge$_{1-x,y}$Sn$_x$Si$_y$ on Ge$_{1-x}$Sn$_x$ buffers, where the strain of the ternary can be tuned by adjusting the Si content in the film or the Sn content in the buffer. We have also started the growth of strained Ge films on Ge$_{1-x}$Sn$_x$ buffers. Theory suggests that tensile Ge layers become direct bandgap materials when the Sn content in the buffer layer exceeds 10 at.%. Other technologically relevant systems we are pursuing include the growth of strained Si on Si-rich Si$_x$Ge$_{1-y}$, where the quality of the Si$_x$Ge$_{1-y}$ buffer is improved through incorporation of a small amount of Sn. Investigations of the thermal stability of these device structures under low-temperature CMOS processing conditions are underway.

**Synthesis and Properties of SiCAlN: A New Wide Bandgap Semiconductor of High Hardness.**

SiC and AlN, normally insoluble in each other below 2000 °C, are combined to form single-phase epitaxial layers at 750 °C on 6H SiC (0001). The key to the successful synthesis is the unique combination of a new low-temperature CVD method utilizing a specifically designed unimolecular source H$_3$SiCN and traditional molecular beam epitaxy of highly reactive fluxes of Al atoms generated form an effusion cell (see equation below).

\[\text{2H}_3\text{SiCN (gas) + 2 Al (atoms) } \rightarrow \text{2SiCAlN (film) + 3H}_2 \text{ (gas)}\]

Stoichiometric SiCAlN material is a wide bandgap semiconductor exhibiting luminescence at 390 nm (3.2 eV) consistent with the predicted bandgap of 3.2 eV. Theoretical structural models of the hexagonal SiCAlN agree well with the experimental microstructure observed by cross sectional electron microscopy studies (see figure 5). An average hardness of 25 GPa was measured for SiCAlN, comparable to that measured for bulk sapphire using the nanoindentation method. Growth of single-phase SiCAlN epitaxial films is also conducted directly on Si(111) between 550 and 750 °C despite the structural differences and the large lattice mismatch (19%) between the two materials. Commensurate heteroepitaxy is facilitated by the conversion of native and thermally grown SiO$_2$ layers on Si(111) into crystalline oxides by in situ reactions of the layers with Al atoms and the H$_3$SiCN precursor, forming coherent interfaces with the Si substrate and the film. High-resolution transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) show that the amorphous SiO$_2$ films are entirely transformed into a crystalline Si-Al-O-N framework in registry with the Si(111) surface. This crystalline interface acts as a template for nucleation and growth of epitaxial SiCAlN. Integration of wide-bandgap semiconductors with Si is readily achieved by this process.

Synthesis of the stoichiometric hybrid SiCAlN is of interest because it combines the novel optical, mechanical, and chemical properties of the binary SiC and AlN constituent systems. Unfortunately the synthetic task is made difficult by the fact that compounds between SiC and AlN can only be made above 1900°C according to the phase diagram using equilibrium methods. Films of (SiC)$_{1-x}$(AlN)$_x$ have been previously deposited by MBE and MOCVD at 1200-1300°C. On account of complexities encountered in the growth process (multiple fluxes, plasmas etc.) as well as the high growth temperatures little progress has been made since these initial studies. Our approach utilizes novel methods and metastable conditions to prepare monocrystalline single-phase SiCAlN at 500-700°C, considerably below the miscibility gap of SiC and AlN. It represents a breakthrough in synthesis of new categories of wide bandgap semiconductors of the main group.
and provides a direct way to grow new quaternary materials in the XCZN family, where X is a Group-IV metal and Z is a Group-III metal. Hypothetical semiconductors with adjustable bandgaps, e.g., GeCAlN, are within reach.

**Epitaxial Growth of Tetrahedral Nitrides on Si via a Superhard, Reflective and Lattice-Matched Metal-Boride Buffer Layers**

ZrB$_2$ has a hexagonal structure with lattice constants $a = 3.169$ Å and $c = 3.530$ Å. The in-plane lattice constant is less than 2% with SiCAlN and the optoelectronic nitrides AlN ($a = 3.11$ Å) and GaN ($a = 3.189$ Å). The thermal expansion coefficients along [1010] on the basal plane are also well-matched between ZrB$_2$ and these materials, particularly GaN. The similarities in structural and thermal properties between ZrB$_2$ and GaN suggest that ZrB$_2$(0001) is an ideal substrate to high quality GaN with low dislocation densities and reduced biaxial strain. Related superhard nitride films of the form SiCAlN, SiCBN, AlB$_4$N$_2$ etc. are likely to grow as epitaxial layers on ZrB$_2$ buffer layers. Here we describe a method to produce for the first time single-crystalline and perfectly epitaxial ZrB$_2$ buffer layers on Si(111). We show that the ZrB$_2$/Si(111) serves as an ideal template for growth high optical quality GaN and SiCAlN films. Ongoing experiments are focused on development of the isostructural ternary borides Al$_{1-x}$Zr$_x$B$_2$, Hf$_{1-x}$Zr$_x$B$_2$ and related nitride derivatives in the Al-B-N, Al-Ga-N and Hf-B-N etc. systems. These materials are highly desirable because of their extreme hardness.

The growth of ZrB$_2$ films on Si(111) substrates at 900°C proceeds via the following reaction:

$$\text{Zr} (\text{BH}_4)_4 (\text{gas}) \rightarrow \text{ZrB}_2 (\text{film}) + \text{B}_2\text{H}_6 (\text{gas}) + 5\text{H}_2 (\text{gas}).$$

A typical ZrB$_2$ buffer layer with a thickness of 50 nm has a metallic appearance and is 100% reflecting. The surface morphology as shown by AFM and XTEM is virtually atomically flat. X-ray rocking curves indicate high crystal quality. Single-crystalline and heteroepitaxial GaN films grown on ZrB$_2$ at 650 °C display luminescence comparable to those of GaN films grown on sapphire by MOCVD. The microstructure of the GaN/ZrB$_2$/Si(111) heterostructure is shown in XTEM image in Figure 6. Remarkably, in spite of the large mismatch in the in-plane lattice parameter between Si(111) where $a = 3.84$ Å and ZrB$_2$ where $a = 3.17$ Å, near-perfect epitaxial growth of ZrB$_2$ is observed. The misfit at the interface is taken up by a pure edge-type dislocation from the insertion of extra{1100} lattice planes along the [1120] direction. No threading dislocations propagating in a direction normal to the substrate are observed. The ratio of the lattice parameters $a(\text{Si})/a(\text{ZrB}_2)$ gives 1.21, which translates into an approximate coincidence of 6 ZrB$_2$ lattice planes with 5 Si lattice planes. The high resolution XTEM image of the interface shown in Figure 7 shows exactly such a 6:5 coincidence. The occurrence of such a “magic mismatch” between hexagonal ZrB$_2$ and Si(111) accounts for the epitaxial growth of ZrB$_2$ even when the lattice mismatch between the two materials is very large. The very sharp transition between Si(111) and ZrB$_2$(0001) at the interface is confirmed by the Z-contrast XTEM image shown in Figure 7. In this image, the contrast is a function of the atomic number Z of the element under observation. One can observe that the epitaxy of the ZrB$_2$ layer is uninterrupted even across an atomic step on the Si(111) substrate.

The ZrB$_2$ buffer layer on Si(111) provides a near lattice-matched template for the growth of epitaxial GaN. Integration of III-nitrides with silicon electronic circuits is readily achieved. The
reflective nature of the ZrB$_2$ surface presents an added bonus to optoelectronic applications of the III-nitrides. Silicon is $\sim$ 45% absorbing for ultraviolet or near-ultraviolet light. However, with the use of ZrB$_2$ buffer layer as a template, the Si(111) substrate becomes 100% reflecting, thus avoiding any loss of emission intensity from the III-nitrides. The ZrB$_2$/Si(111) substrate offers many distinct advantages in both microelectronic and optoelectronic applications of group III nitrides, the most important of which is the integration with silicon electronics.