Synthesis by Laser Ablation and Characterization of Pure Germanium–Carbon Alloy Thin Films

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Thin films of pure germanium-carbon alloys (Ge_xC_{1-x} with seven different compositions ranging from $x = 0.0$ to $x = 1.0$) have been grown on Si and Al_2O_3 substrates by pulsed laser ablation. Each film was grown from a single target composed of a physical mixture of elemental Ge and graphite, and in each case, the composition of the alloy produced was close to that of the target mixture. The films were analyzed by X-ray θ–2θ diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), conductivity measurements, and optical absorption spectroscopy. The analyses of these new materials showed that the alloys of all compositions were amorphous, free of contamination, and uniform in stoichiometry. By changing the film composition, the optical bandgap of these semiconducting films was varied from 0.00 to 0.85 eV for $x = 0.0$ to 1.0, respectively. The line shape of the C KVV peak in the Auger spectra revealed that the carbon atoms in the alloy films were present in both sp^2 and sp^3 hybridizations.

I. Introduction

The group IV elements C, Si, Ge, and Sn are all semiconductors when they are tetrahedrally bonded in the diamond lattice structure. A gap, which ranges from 0.08 eV for Sn to 5.45 eV for diamond, splits the valence and conduction bands that are derived from sp^3 hybridized orbitals. Thus, it is natural to explore the compounds and alloys of group IV elements to see if it is possible to synthesize new materials with an arbitrary bandgap in the range above by controlling the *stoichiometry*. Carbon containing compounds may also have delocalized π states that result from sp^2 hybridized C orbitals, which could extend the bandgap of group IV alloys down to 0 eV depending on the bonding *geometry*.

There are two well-known examples of binary group IV systems. The first is the stoichiometric compound SiC, which has only one stable composition but can exist in a large number of different structural polymorphs.[1] Each polymorph of SiC has a set of unique properties, but the range of bandgaps available in this system is very restricted. An amorphous hydrogenated version of SiC, $Si_{1-x}C_x$:H is an important material for constructing solar cells and has an optical bandgap that varies from 1.8 to 3.0 eV.[2] The second system is the nearly continuous range of solid solutions formed by Si and Ge, for which the bandgap can be varied from 0.65 to 1.4 eV in crystalline materials. A high degree of control has been reached in this alloy system by growing epitaxial layers with different compositions, and thus different lattice constants, on top of each other and thereby making use of stresses and strains in the films to tune the electrical properties of the layers (bandgap engineering).[3] The incorporation of small (~1%) amounts of substitutional C into Si–Ge alloys has also been used to compensate for strain in epitaxial films.[4] However, it is still true that the range of bandgaps available in the Si–Ge alloys is small compared to those achieved in the alloys of compound semiconductors.

Compounds and alloys involving group IV elements that are not neighbors in the periodic table would appear to provide a broader range of tunability in bandgap and other properties. Unfortunately, except for the important systems noted above, there are no other thermodynamically stable phases involving pairs of group IV elements.[5–7] However, the potential for new properties in group IV alloys is so great that even metastable systems could be useful, especially considering that diamond itself is a metastable phase. In particular, alloys of Ge and C are of interest because of their potential in photothermal[8] and photovoltaic[9] applications. Alloying with C could improve the structural properties of Ge, and result in a material with a bandgap tunable over a very wide range with the lower limit considerably below that of amorphous Si–C alloys.[8]

Synthesizing metastable Ge–C alloys requires that significant kinetic difficulties be overcome. The melting point of C is about 3550 °C whereas that of Ge is only 980 °C.[5–7] In a liquid precursor to a Ge/C alloy, the C solidifies and phase separates long before the Ge can solidify.[3,10] Thus, only gas-phase routes in which the condensate is rapidly quenched appear to have a chance of producing a chemically homogeneous material in a useful form. The pioneering work in the preparation of Ge–C alloy thin

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films was done by Anderson and Spear in 1976.[11] They prepared amorphous alloys of Ge and C by glow discharge decomposition of mixtures of ethylene and either 10% or 20% germane. Films were deposited on fused quartz or Corning 7059 glass disk substrates at temperatures of 420, 425, 500, and 560 K. They performed electrical and optical measurements and found that the films were semiconducting, with optical bandgaps of the order of 1.5 eV. There was a trend toward a lower electronic activation energy and a higher conductivity with increasing germane concentration and with increasing substrate temperature. There was no report on the hydrogen concentration in their films, but since the substrate temperatures were low, the films most likely contained significant amounts of hydrogen.

Booth and Voss[8] produced films by chemical vapor deposition from pyrolytic decomposition of acetylene–germane mixtures with a carrier gas of either He or H_2/He mixtures at substrate temperatures of 450 and 550 °C and with $C_2H_2/(GeH_4 + C_2H_2)$ ratios from 0% to 75%. They observed a *decrease* of the value of the refractive index and a *red shift* of the profile of the absorption coefficient relative to the values of polycrystalline germanium as the acetylene gas fraction *increased*. Their X-ray diffraction measurements revealed strong polycrystalline germanium peaks for low carbon content, but the intensity of the peaks decreased significantly as the acetylene gas fraction increased. There was no report on the hydrogen concentration or the optical bandgap of their films. Shinar et al.[9] grew hydrogenated amorphous Ge–C alloy films by rf sputtering of a polycrystalline Ge target in a mixture of Ar, H_2, and C_3H_8. Most of their films had a C/Ge ratio ≤ 0.15 as determined by Auger electron spectroscopy. The optical gap of the amorphous $Ge_{1-x}C_x$:H films ranged from 0.85 to 2.3 eV, with the highest value corresponding to pure amorphous hydrogenated carbon. The hydrogen concentration in the film was reported to be equal to or larger than the carbon concentration. Since these early studies, several other groups have produced films of sputtered Ge–C:H for different applications.[12-17] There have also been several studies of the C–Si–Ge:H alloy system,[18-21] mainly for applications in the area of photovoltaic devices. Girginoudi and Thanailakis[18] reported that amorphous $(SiC)_xGe_{1-x}$ thin films prepared by rf sputtering have optical bandgaps which vary from 1.0 to 2.25 eV depending on the Ge content and H_2 partial pressure.

All previously reported Ge–C[8-17] and C–Si–Ge[18-21] alloy films containing substantial amounts of C were amorphous and also had high concentrations of hydrogen, since they were prepared by sputtering. To determine the properties of pure metastable alloys and compare them with the hydrogenated materials, we grew Ge–C alloy films by laser ablation[22] from a single target containing mixtures of the pure elements. This technique has been used in the past primarily to *grow* high quality (usually epitaxial) films from targets consisting of the desired compounds,[22] but in this case it was chosen as the best way to *synthesize* a series of particularly challenging metastable alloys. Films of Ge_xC_{1-x} with seven different compositions from $x = 0.0$ to 1.0 were grown on Si and sapphire substrates under high-vacuum conditions and then characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), conductivity measurements, and optical absorption spectroscopy.

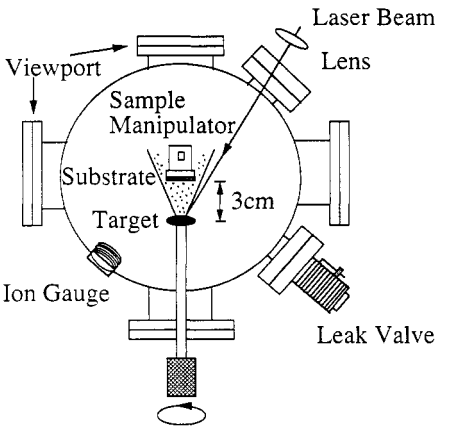

Figure 1. Schematic diagram of the laser ablation system used in this work.

II. Experimental Procedure

Figure 1 shows a schematic diagram of the laser ablation system. A standard stainless steel belljar was pumped by a turbomolecular pump and an ion pump. The base pressure inside the chamber was 2×10^{-9} Torr after a quick bakeout, and during the film deposition, the pressure rose to 1×10^{-6} Torr. Although the system could operate under ultrahigh-vacuum conditions, we chose to maximize the number of samples and thus did not bake the system thoroughly between growth experiments. This operating mode was reasonable for our experiments because the background level of contaminants in our films was below our detection level.

The targets were prepared from Ge and graphite powders, with purities of 99.999% and 99.9995%, respectively, which were weighed and mixed to produce the desired compositions. The powders were mixed and then ground with a mortar and pestle inside a drybox to homogenize the mixtures and to avoid air contamination. The mixtures were pressed into pellets under a force of 10 000 lbs. The resulting targets were disks 13 mm in diameter and 1 mm thick. Target preparation required a great deal of practice and care, since the different densities of the Ge and graphite would allow them to separate during handling and produce a nonuniform pellet. The upward facing side of the pellets from the die were always used as the ablation target.

The ablating laser was a Lamda-Physik, Inc., Model EMG102 MSC, using an ArF gas mixture to produce a wavelength of 193 nm. For all the films reported here, the pulse energy was 160 mJ and the repetition rate was 10 Hz, although other experiments showed that the final films were not very sensitive to these parameters. The laser beam was focused through a quartz window to a spot size approximately 1 mm × 1 mm onto the target, which was rotated at 25 rpm to avoid texturing the surface of the pellet. Before depositing the film, the substrate was rotated away from

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the target and the laser was turned on for half a minute to clean the surface of the pellet by ablation.

Films were deposited both on Si and on sapphire substrates. The Si substrate was pretreated following the procedure described in ref 23 and was then resistively heated in the high vacuum chamber to 1100 °C for 3 min to evaporate any oxide off the surface. The sapphire substrates were first etched in a 49% HF acid solution for 1 min before mounting on the sample holder and placing in the vacuum chamber. The sapphire was then heated to 1200 °C in vacuo by passing a current through a piece of tungsten foil held at the back of the sample to eliminate any carbon contamination from the surface.

The distance from the target to the substrate was 3 cm. The substrate temperature was held at 450 °C, as measured by an infrared pyrometer, during the film growth. The samples were transferred into a drybox immediately after growth to minimize air contamination of the film surfaces and stored in the drybox for subsequent analyses. All the samples reported here were smooth and specular when examined under an optical microscope. The film thicknesses, which were measured by a Dek Tak system, ranged from about ~500 Å for films grown for optical absorption experiments to ~0.6 μm for other film characterization experiments. The growth rates of the films were about 120 Å/min or 0.2 Å/laser pulse. To avoid depositing particles on the substrate, the laser beam was focused at an off-center position on the target. The rotation of the target imparted a tangential component to the velocity of the ablated material that was small compared to the velocity of the atomic and molecular species but large enough compared to the large particles that they missed the substrate surface.

The XRD experiments were performed using a Crystal Logic θ–2θ diffractometer with a Cu X-ray source. The samples were all nominally 6000-Å-thick films deposited onto sapphire substrates. To obtain a high detection sensitivity for small amounts of crystalline phases, a scan time of 3.5 h was used for each sample.

The electron spectroscopic measurements were performed in a Kratos XSAM800 system equipped with a 127-mm-radius hemispherical analyzer. The system has a dual anode (Al/Mg) source for XPS measurements and a 10-keV electron gun (resolution approximately 2000 Å) for scanning electron microscopy (SEM) and AES measurements. XPS was used to examine the surface contamination and to analyze the chemical compositions of the films. The electron-excited C KLL Auger spectra were collected on the thin films of different compositions in the pulse counting mode, and then the spectra were differentiated numerically to achieve the spectral resolution of the analyzer, in this case about 0.8 eV. The same type of AES spectra were also collected on a freshly cleaved highly oriented pyrolytic graphite (HOPG) sample, a SiC single-crystal sample from Atomergic Chemetals Corp., and a diamond single crystal to compare with the AES spectra of the laser-deposited films.

The conductivity of the thin films on sapphire was measured by the four-point probe method. Four Ag strips to serve as contacts were evaporated onto each premasked film surface in an evaporator, and the probe wires were connected to the contacts with silver paste. The samples were then cemented onto a holder, capped and inserted into a liquid He tank where there was a temperature gradient that ranged from 100 K to nearly room temperature. The outer two probes were used to pass current from a regulated power supply through the sample, and the inner two probes were connected to a voltmeter. The optical absorption spectra were obtained for 500-Å-thick samples grown on sapphire substrates with a Hewlett-Packard 8451A diode array spectrophotometer. The spectra were collected in the transmittance mode, with the wavelength ranging from 190 to 820 nm (or from 6.54 to 1.52 eV).

III. Results and Discussion

We use Ge_y/C_{1-y} ($0 \le y \le 1$) to express the composition of an ablation target composed of a powder mixture of Ge and C. Figure 2A,B shows θ–2θ XRD patterns for a bare sapphire substrate and for a 6500-Å-thick film deposited on sapphire from a $Ge_{0.2}/C_{0.8}$ target, respectively. The two diffraction patterns are identical except for a very small Ge(111) peak at 27.2° in the X-ray diffraction pattern for the film, which indicates that the thin film that was examined was mostly amorphous with a very small amount of microcrystalline Ge. Similar results were obtained for the other thin films grown on sapphire substrates. In a subsequent experiment, the same thin film sample was annealed at 450 °C for 2 h. The XRD pattern collected, as shown in Figure 2C, is very similar to that of Figure 2B. The same film was then annealed again at 580 °C for 2 h, and another XRD pattern was collected. This new pattern, as can be seen in Figure 2D, showed a more intense Ge(111) peak, indicating that more Ge in the film had crystallized. This experiment showed that our XRD system has the sensitivity to detect crystalline phases if they are present in the thin deposited films and also that the deposited metastable alloys are stable up to at least 450 °C for extended periods of time and eventually decompose to yield the elements after prolonged annealing to sufficiently high temperature.

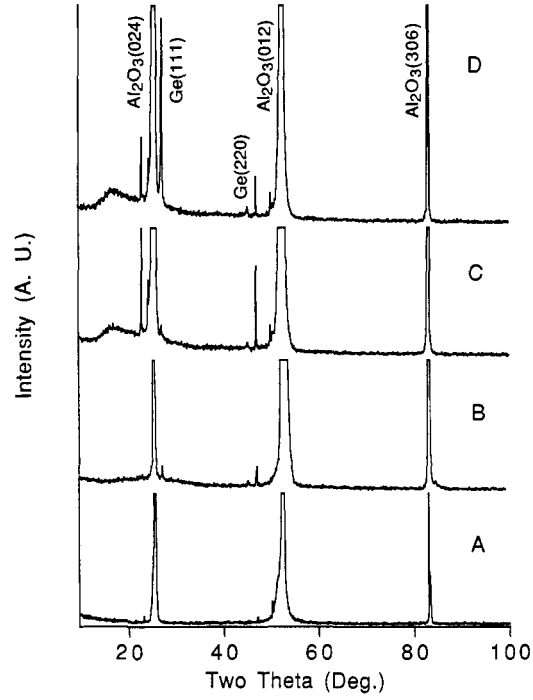

Figure 2. X-ray θ–2θ diffraction (XRD) patterns for (A) a bare Al_2O_3 substrate, (B) a thin film sample grown from a $Ge_{0.2}/C_{0.8}$ target onto Al_2O_3 substrate, (C) the same film after annealing at 450 °C for 2 h, and (D) the same film after annealing again at 580 °C for 2 h.

To detect the presence of any contaminants in and to determine the compositions of the samples, we performed XPS experiments on films grown on Si substrates, which were used to eliminate sample charging during the electron spectroscopy measurements. These films had thicknesses comparable to those of the films deposited on sapphire substrates for the conductivity measurements. Figure 3A shows the X-ray photoemission spectrum for the film as deposited from a $Ge_{0.2}/C_{0.8}$ target and then transferred through air from the growth to the analysis chambers. Figure 3B shows the X-ray photoemission spectrum for the same film after the surface was sputter cleaned by Ar ion bombardment for 10 min at a beam energy of 3.5 keV. The small amount of oxygen impurity detected on the surface of the as-deposited and transferred film was

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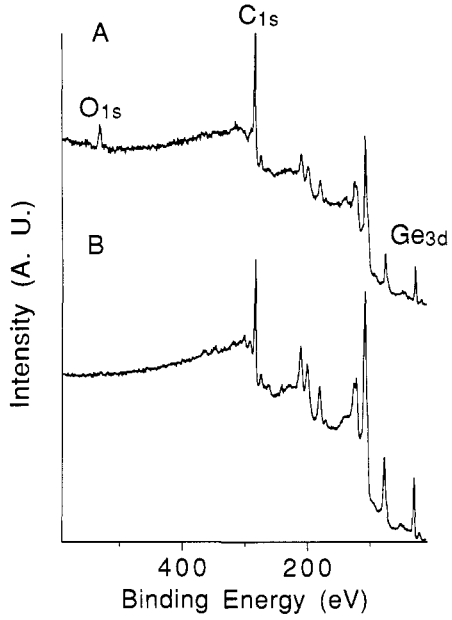

Figure 3. X-ray photoelectron spectroscopy (XPS) data for (A) the thin film grown from the $Ge_{0.2}/C_{0.8}$ target on the Si substrate, and (B) the same thin film after the film surface was sputter cleaned by Ar ion bombardment for 10 minutes at a beam energy of 3.5 keV.

probably introduced when the sample was briefly exposed to air. After sputter cleaning, the oxygen and any other impurities were below the XPS detection limit. Similar results were obtained for all other films with different compositions.

We have also determined approximate stoichiometries for all the films grown on Si surfaces by quantitative analysis of the XPS data. The compositions were derived by measuring the areas of the C_{1s} and Ge_{3d} peaks in the XPS spectra of Figure 4 and using published sensitivity factors[24] to calculate the relative atomic concentrations. These are estimates, since the sensitivity factors from ref 24 were determined for a cylindrical mirror analyzer (CMA). However, we have consistently found these sensitivity factors to yield answers to within 10% for samples with known composition. The Ge-to-C peak ratios in the spectra also changed by no more than 10% for any of the samples after 10 min of sputtering and then reached a constant value thereafter. Taking these factors into account, the measured compositions of the films were within experimental error of the known compositions of the targets, indicating nearly congruent evaporation and identical sticking coefficients for the ablated Ge and C. Some samples were sputter profiled through the entire thickness of the films with no significant variation detected in the film stoichiometries. The target and corresponding film compositions are listed in Table I. The most important point to note here is that the stoichiometries of the films can be varied systematically simply by changing the composition of the target.

Auger spectra collected at various locations across the surfaces of the films showed that they were also laterally homogenous, since the intensity ratios of the C and Ge AES peaks were essentially independent of position. The C KLL AES peak line shape is extremely sensitive to the

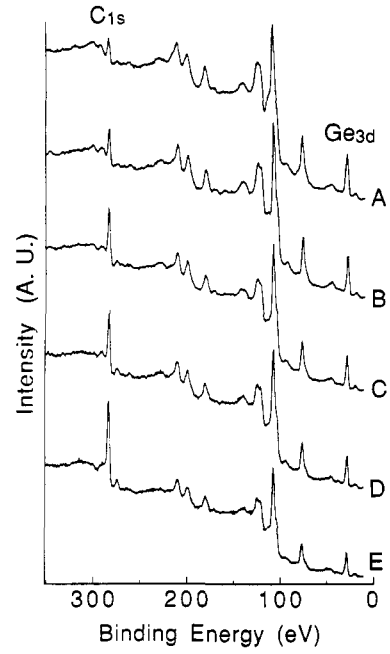

Figure 4. XPS spectra collected from films grown from targets of mixtures of carbon and germanium in different concentrations. The targets used, from top to bottom, were $Ge_{0.8}/C_{0.2}$, $Ge_{0.6}/C_{0.4}$, $Ge_{0.5}/C_{0.5}$, $Ge_{0.4}/C_{0.6}$, and $Ge_{0.2}/C_{0.8}$. The approximate film compositions determined from quantitative analysis of the XPS data, from top to bottom, were $Ge_{0.7}C_{0.3}$, $Ge_{0.5}C_{0.5}$, $Ge_{0.4}C_{0.6}$, $Ge_{0.3}C_{0.7}$, and $Ge_{0.2}C_{0.8}$, respectively.

Table I. Values of the Target Compositions and the Corresponding Film Compositions As Analyzed by XPS

target composition	XPS film composition	target composition	XPS film composition
$Ge_{0.8}/C_{0.2}$	$Ge_{0.7}C_{0.3}$	$Ge_{0.4}/C_{0.6}$	$Ge_{0.3}C_{0.7}$
$Ge_{0.6}/C_{0.4}$	$Ge_{0.5}C_{0.5}$	$Ge_{0.2}/C_{0.8}$	$Ge_{0.2}C_{0.8}$
$Ge_{0.5}.C_{0.5}$	$Ge_{0.4}C_{0.6}$		

hybridization of carbon,[25] much more so than the XPS line shape or chemical shift. This provides a simple way of investigating how carbon atoms are bonded in the deposited films. To obtain this information, AES data were collected for Ge–C alloy thin films grown on Si substrates and compared with the C KLL spectra for materials containing carbon with known hybridizations, i.e., a diamond single-crystal sample, a silicon carbide single-crystal sample, and a highly ordered pyrolytic graphite (HOPG) sample. The line shapes for the different forms of carbon are shown in Figure 5. For diamond, where the carbon atoms are bonded through sp^3 hybridized orbitals, the positive part of the AES spectrum has one peak with a shoulder to its left and the negative part of the spectrum has one large peak and one small peak at 300 eV kinetic energy. For graphite, where carbon atoms are bonded through sp^2 hybridized orbitals, the positive part of the spectrum has two peaks and the negative part of the spectrum has one big peak and one small peak to its left. Since carbon atoms are also sp^3 bonded in a SiC single crystal, the C KLL AES peak line shape for carbon in SiC is similar to the C KLL AES peak line shape for carbon in diamond. The oxygen peak shown in the AES spectrum for SiC is a bulk impurity, since the sample surface was cleaned by a combination of mechanical polishing, chemical etching with 49% HF acid solution and Ar ion sputtering

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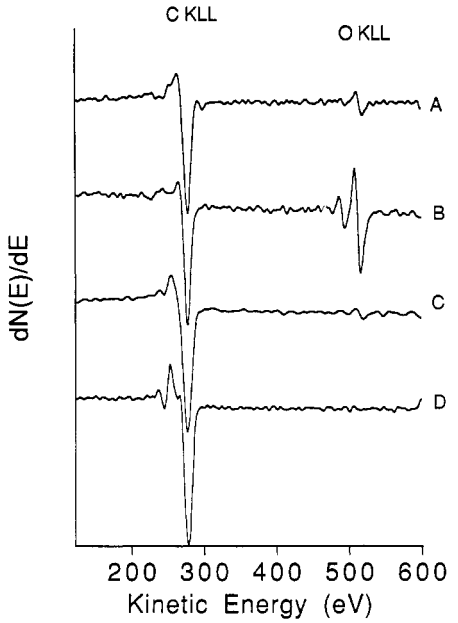

Figure 5. Comparison of the C KLL AES peak line shape collected for different materials containing carbon: (A) diamond single crystal, (B) SiC single crystal, (c) $Ge_{0.2}C_{0.8}$ thin film, and (D) a freshly cleaved HOPG sample.

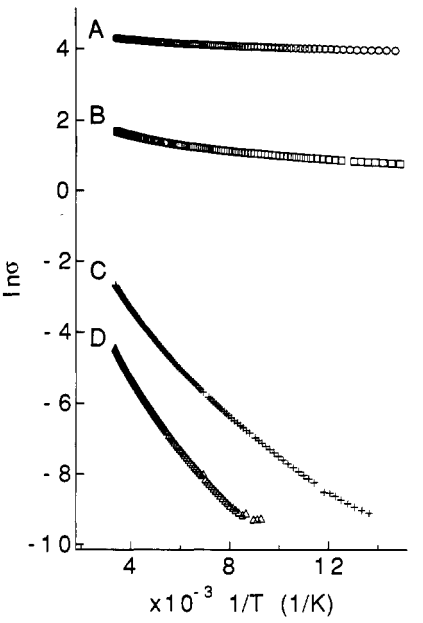

Figure 6. Conductivity measurements for the alloy films plotted as ln σ vs $1/T$: (A) $Ge_{0.2}C_{0.8}$, (B) $Ge_{0.3}C_{0.7}$, (C) $Ge_{0.4}C_{0.6}$, and (D) $Ge_{0.5}C_{0.5}$.

at 3.5 eV for 1 h, all with no significant oxygen reduction. For the thin film sample grown from the $Ge_{0.2}/C_{0.8}$ target, as shown in Figure 5, the C KLL Auger line shape is a mixture of the line shapes of diamond and graphite. The same type of C KLL AES peak line shape was observed for all other thin films with different compositions. Therefore, we conclude that the thin films contain a mixture of sp^2 and sp^3 hybridized carbon, consistent with the amorphous structure of the films.

The conductivity of the films decreased with decreasing temperature for all the samples examined, which indicates that all the films were semiconducting. As the carbon concentration decreased in the films, the room-temperature conductivity of the films decreased. The results of the conductivity measurements were plotted as ln (σ) vs $1/T$ as shown in Figure 6, where σ is the conductivity and T is the temperature in kelvin, in order to obtain a crude estimate of the electrical activation energy E_σ:[26]

$$\ln \sigma = \ln \sigma_0 - E_\sigma/kT \quad (1)$$

where σ_0 is a constant and k is the Boltzmann constant. The values of E_σ were obtained from the slopes of the curves shown in Figure 6 for the films measured, and are listed in Table II to compare with previous determinations for hydrogenated films.[8-11]

The optical absorption data were fitted to the Tauc relation:[27,28]

$$(\alpha h\nu)^{1/2} = B(h\nu - E_{opt}) \quad (2)$$

where α is the absorption coefficient measured with the spectrophotometer, h is Planck's constant, ν is the photon frequency E_{opt} is the optical band gap (in our case, we consider the film thickness to be included in the constant B). The intercept of the line formed by plotting the data according to eq 2 with the abscissa of the plot is the value of E_{opt}. As shown in Figure 7, the optical bandgap obtained for the laser-deposited Ge thin film was 0.85 ± 0.05 eV, which is close to the value of 0.89 eV reported previously for amorphous Ge.[26] The optical bandgap for the laser deposited C film was 0.0 ± 0.05 eV, and the E_{opt} values for the alloy films, which are listed in Table II, were intermediate between the two elemental films.

Table II. Room-Temperature Experimental Values of E_{opt} and E_σ for Amorphous Ge–C Alloy Thin Films Grown by Laser Ablation

thin films	E_σ (eV)	E_{opt} (eV)	thin films	E_σ (eV)	E_{opt} (eV)
Ge		0.85	$Ge_{0.3}C_{0.7}$	0.017	0.20
$Ge_{0.7}C_{0.3}$	N/A	0.78	$Ge_{0.2}C_{0.8}$	0.007	0.10
$Ge_{0.5}C_{0.5}$	0.121	0.70	C		0.00
$Ge_{0.4}C_{0.6}$	0.098	0.65			

It is important to note that the Tauc plots indicate only a single bandgap for each film rather than a combination of two or more different bandgaps, so that the material in each film is compositionally homogeneous. To demonstrate this point, we simulated transmittance vs wavelength data for a 50:50 mixture of elemental Ge and C from the experimental transmittance values of our pure elemental films:

$$T(h\nu)_{Ge/C} = T^{1/2}(h\nu)_{Ge} \times T^{1/2}(h\nu)_C \quad (3)$$

where $T(h\nu)_{Ge/C}$ is the transmittance for the simulated mixed phase film, and $T(h\nu)_{Ge}$ and $T(h\nu)_C$ are the experimental transmittance values for the Ge and C films, respectively. The simulated transmittance vs. wavelength data were then analyzed with the Tauc relation, and the plot obtained for the phase mixture is shown in Figure 8, which also contains the experimental Tauc plots for the pure Ge and C films and the film grown from the $Ge_{0.5}/C_{0.5}$ target. The Tauc plot of the simulated mixed phase shows a significant curvature over the region plotted, indicating that there are two different bandgaps present, whereas all of the experimental plots are much closer to a straight line.

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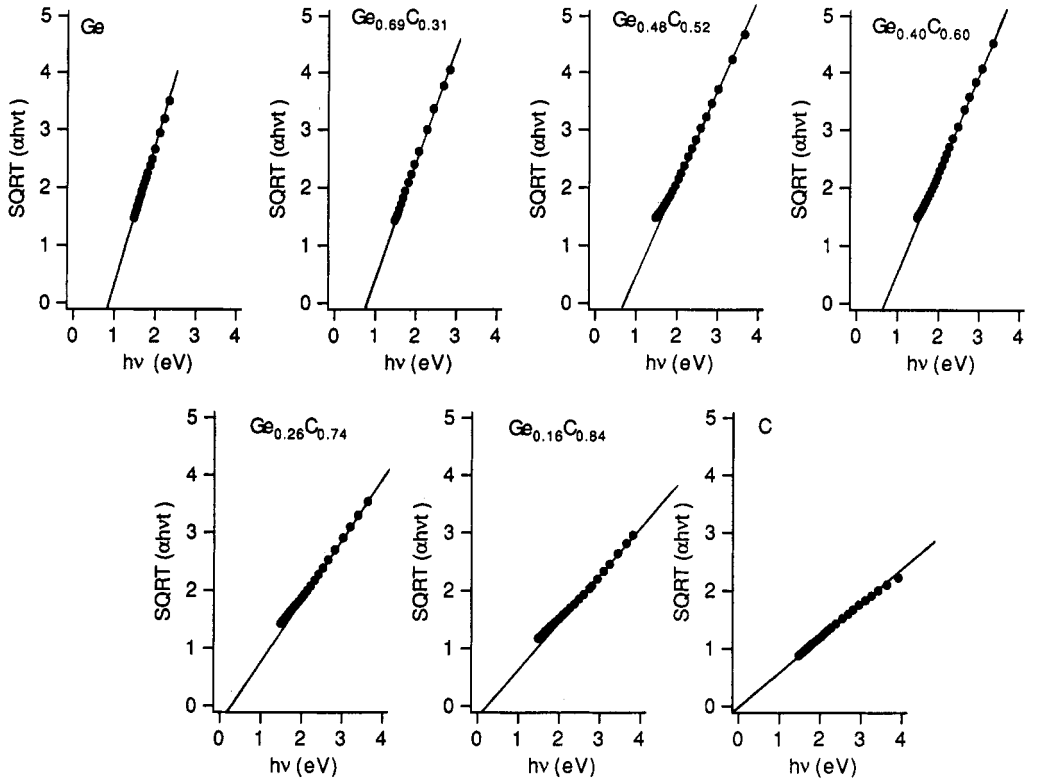

Figure 7. Optical absorption in Ge_xC_{1-x} ($0 \le x \le 1$) thin films grown by laser ablation plotted as $(\alpha h\nu t)^{1/2}$ versus photon energy $h\nu$. The x intercepts of the lines give the optical bandgaps of the films.

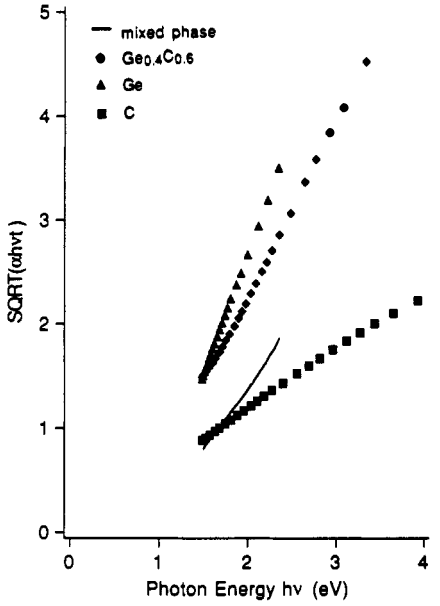

Figure 8. Simulated Tauc plot for a mixed phase of Ge and C, as well as experimental Tauc plots for the Ge, C, and $Ge_{0.4}C_{0.6}$ thin films.

As shown in Table II, both the activation energies and the optical bandgaps of the films decrease when the carbon concentration in the thin films increase, which means that we can tune the bandgaps of Ge_xC_{1-x} by simply changing the stoichiometries of the films. The activation energies obtained from the conductivity measurements were much smaller than the optical bandgap values, which is the usual situation for amorphous semiconductors.[29] There is a continuum in the gap between the valence and conduction band edges available for current transport via hopping among the localized states. On the other hand, optical excitations still primarily occur across the gap, and in fact the density of states is piled up such that the optical gap for an amorphous material is somewhat larger than that for the corresponding crystalline material.

Because of the substantial number of carbon atoms in the films that are sp^2 hybridized, E_{opt} of the films varies between 0.00 and 0.85 eV, which are the E_{opt} values for amorphous carbon and germanium, respectively. This runs counter to expectations in the literature,[8,9] where it was assumed that such alloys would be crystalline with all the C sp^3 hybridized so that the bandgap would range between that of crystalline Ge (0.65 eV) and diamond (5.45 eV). The trends observed in the electrical and optical bandgaps of the pure Ge–C alloys produced in this study with increasing C concentration are just opposite to those for most of the hydrogenated films grown by sputtering,[8,9] presumably because the H acts to terminate any dangling bonds in the films and thus greatly reduce the concentration of sp^2 hybridized C atoms in the alloys.

IV. Conclusions

Thin films of pure germination–carbon alloys (Ge_xC_{1-x}, with $0 \le x \le 1$) have been grown on Si and Al_2O_3 substrates by pulsed laser ablation. The structural and chemical analyses of this new material showed that films of all compositions were amorphous, free of contamination and uniform in composition. By changing the film composition, the optical bandgap of these semiconducting films was varied from 0.00 to 0.85 eV for $x = 0.0$ to 1.0, respectively. This trend is just opposite to that observed for hydrogenated Ge–C films, which also have absolute bandgaps about a factor of 2 higher than the pure alloys.[8,9] The C KLL

(29) Blakemore, J. S. *Solid State Physics*; Cambridge University Press: Cambridge, 1985; p 351.

Auger spectra of the pure Ge–C alloys reveal the presence of both sp^3 and sp^2 hybridizations. The presence of the sp^2 C apparently causes the bandgap of amorphous Ge–C alloys to decrease with increasing C concentration.

Laser ablation can be used for the direct synthesis of metastable alloys as thin films by vaporizing the constituent elements from a mixed phase target. At sufficiently high powers, all materials are ablated with essentially equal efficiency.[22] The rapid cooling of the ablated material that contacts a substrate will form an intimately mixed alloy or compound as long as the surface diffusion lengths are not long enough to allow significant phase separation to occur.

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