The MBE Growth and Electronic Structure of α-Sn_xGe_{1-x} Alloys

Hartmut Höchst, Michael A. Engelhardt and
David W. Niles*
Synchrotron Radiation Center
University of Wisconsin-Madison
Stoughton, WI 53589-3097

Abstract

The MBE growth and electronic structure of α-Sn_xGe_{1-x} alloy films were studied with RHEED and angle resolved synchrotron radiation photoemission spectroscopy. Doe to an increased interfacial reactivity, CdTe substrates are not suitable for the epitaxial growth of homogeneous films with x>0.1. Alloy films with good crystalline quality can be grown on Ge(100) substrates at ~400 C. The expected closing of the alloy band gap is confirmed by photoemission data which show the shift of the Γ_8 valence band maximum from ~0.6 eV in Ge(100) to ~0.16 eV below E_F in α-$Sn_{0.48}Ge_{0.52}$

I. Introduction

Alloys of Ge with Sn can be expected to have electronic properties which make them very attractive for novel infrared detectors. The incorporation of Sn, a semimetal in the diamond structured α-phase, should close the band gap of Ge and would thus allow the gap to be tailored over a wide range of great technological interest[1,2].

Assuming a linear relationship between the band structure of both components, the indirect Γ_8-L_6 gap of Ge would turn into a direct Γ_8-Γ_7 gap of E_g~.55 eV for x~0.2. For Sn concentrations above x~0.2 the gap would close further reaching the zero gap condition (crossover point of the Γ_8 valence band and the Γ_7 conduction band) at x~0.65. Due to the greatly reduced polar scattering, α-Sn/Ge alloys may develop carrier mobilities which are considerably higher then those in similar isoelectronic compounds such as $Hg_xCd_{1-x}Te$.

Unfortunately major problems exist in the preparation of the suggested α-Sn/Ge alloys. First, bulk α-Sn is only stable at temperatures below ~13.2 C, and second, Sn is nearly immiscible in Ge[3,4]. Conventional growth methods working under thermodynamic equilibrium conditions are thus not suitable for the fabrication of metastable α-Sn/Ge alloys. However, we have shown that MBE, which is a non equilibrium growth technique, can produce α-Sn films that are stable to temperatures well above 100 C[5,6]. Heteroepitaxial α-Sn films grown up to ~5000 Å thick on CdTe(100) substrates where of high crystalline perfection and good electronic quality. Low temperature transport measurements[7] revealed n-type behavior with $n_d \sim 3 \cdot 10^{17} cm^{-3}$ and mobilities of $\sim 4 \cdot 10^4$ $cm^2/Vsec$. At present it is unclear, whether these parameters are the intrinsic properties of α-Sn, or if they could be improved further through the growth of buffer layers with higher structural quality than that of the presently available commercial CdTe substrates. One can also speculate that the addition of Ge may actually help to further increase the α–β phase transition temperature and thus allow the operation of potential α-Sn/Ge devices under moderately elevated temperatures.

This paper reports MBE growth studies of α-Sn_xGe_{1-x} alloys on CdTe(100) and Ge(100) substrates. We used reflection high energy electron diffraction (RHEED) and *in situ* synchrotron radiation photoemission spectroscopy to investigate the structural and electronic properties of the MBE films.

II. Results and Discussion

The structural quality of MBE grown films depends critically on the lattice match between substrate and epitaxial overlayer. Lattice mismatch causes strained overlayer growth. The critical thickness of metastable strained films has been shown to exceed the calculated thermodynamic equilibrium limits by more then two orders of magnitude. Of particular importance in the area of strained layer epitaxy was the work by Bean et al.[8] demonstrating that thin films of defect free Ge_xSi_{1-x} layers can be grown in registry with Si substrates for misfits as large as ~3 %.

The incorporation of lattice mismatch related strain will certainly be a disadvantage and contribute

to the instability of the thermodynamically unstable α-phase of Sn/Ge alloys. Substrate materials which are isomorphic and closely lattice matched to α-Sn are InSb and CdTe. At room temperature the lattice constant of α-Sn is slightly larger than that of InSb and CdTe with a 0.14% misfit with InSb and a 0.1% mismatch with CdTe. We have studied the effect of lattice mismatch on the critical thickness of epitaxial films by adding certain amounts of Ge to α-Sn films. Assuming Vegards law for the alloy lattice constant, the incorporation of Ge would create a ~0.13% lattice misfit per added percent Ge. Since the lattice constant of the alloy is smaller than those of the substrates the epilayers will be under tensile stress. The accumulation of strain energy and it's release into misfit dislocations causes the break down of the metastable epitaxial phase at the critical film thickness.

Figure 1 shows the boundary curve which separates the growth region of the pure α-phase from that of the mixed α+β phase . The phase analysis is based on the appearance of the metallic β-phase in the valence band photo emission spectrum. It is clear that the phase analysis based on photoemission experiments does not present the same accuracy and sensitivity as an x-ray diffraction experiment utilizing a Read Camera or double crystal rocking curve analysis.

Photoemission spectroscopy, however, provides us with a stability curve which reflects at least the trend of the critical thickness as a function of lattice misfit. It should be noted that the curve shown in Fig.1 does not solely reflect the strain effect but also describes the phase separation and clustering effects related to the surface mobilities of the deposited atoms at a particular substrate temperature. As can be seen from Fig1. the critical thickness peaks for films which are nearly lattice matched and drops off fast for larger misfits in a fashion similar to those reported for other metastable systems[8].

Core level intensity measurements also indicate surface segregation. For the alloy growth on CdTe(100) substrates, where the negative misfit iforces the epilayer to grow under tensile strain, we find Ge enrichment in the surface layers. Whereas growth on Ge(100), which results in a compressed epilayer, forces the surface region to be Sn rich. The deviations of the surface composition versus the lattice mismatch are shown in Fig.2. The data points were obtained from alloy films 200-400 Å thick at $T_{sub.}$=25 C.

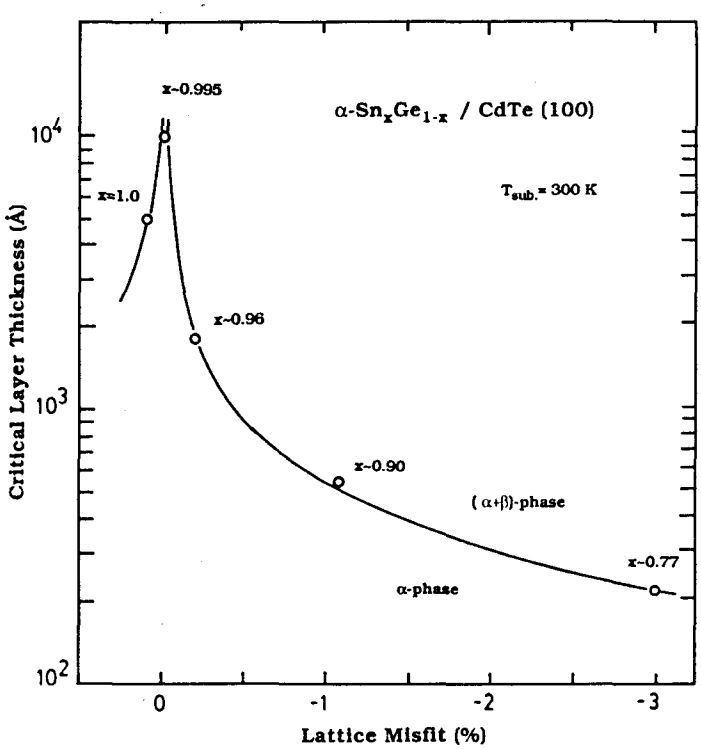

Fig.1: Critical layer thickness as a function of lattice mismatch for α-Sn_xGe_{1-x} grown on CdTe (100)

The plotted ratio between the concentration in the deposited film c_{alloy} versus the concentration in the flux c_{beam} shows a variation which is easy to interpret. In order to minimize the interfacial strain, the initial growth at the substrate interface is enriched with the component that is better lattice matched to the substrate. Recent stochastic Monte Carlo calculations simulated the strained epitaxial growth of Ge_xSi_{1-x} on Si(100) and found the same trend[9]. Above a certain critical concentration, the overlayer growth with defects which are the trigger to initiate a surface segregation of Ge. With the onset of defect formation there is also an increase in surface roughness .

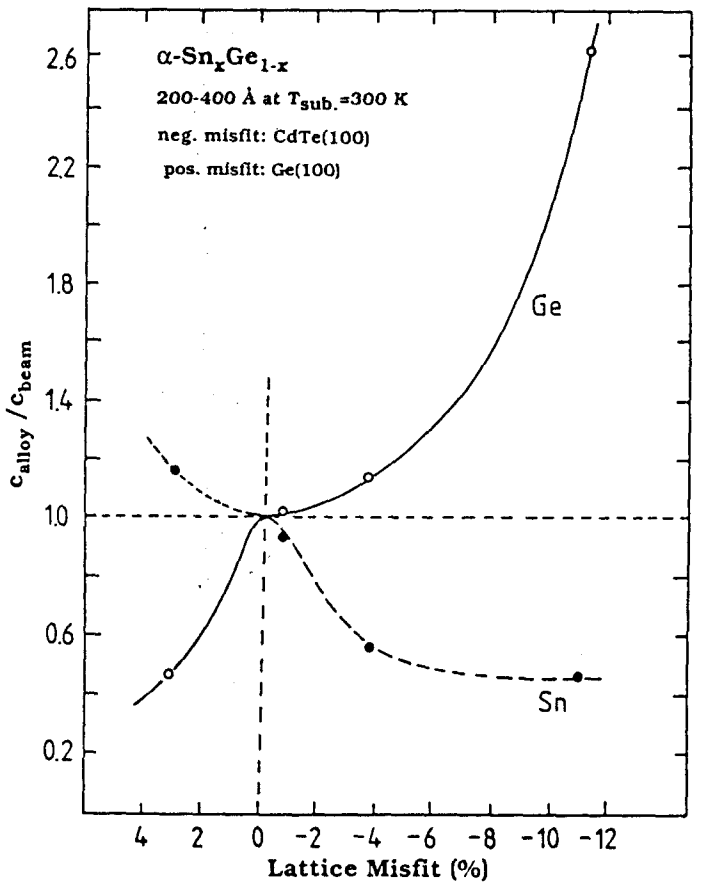

Fig.2: Normalized alloy concentration at the surface as a function of lattice misfit

Higher growth temperatures offer increased surface mobility and reduce the tendency to form clusters. However one must keep in mind that higher deposition temperatures also increase the chance for interfacial reactivity. Both processes are in competition and need to be carefully balanced in cases where reactions with the substrate are likely.

In order to study the effect of increased surface mobilities we also investigated the alloy growth at elevated substrate temperatures. Figure 3 shows a set of valence band photoemission data of a film 500 Å thick of $Sn_{0.75}Ge_{0.25}$ as a function of growth temperature. Since the alloy film is thicker then the critical value of ~200 Å, the room temperature spectrum shows a Fermi level emission which is typical for an alloy with a precipitated β-Sn phase[10]. According to the Fermi level emission the amount of the β-Sn phase decreases at growth temperatures ~200 C. At the same time we observe considerably sharper emission features deeper in the valence band which improve with increasing substrate temperature. Alloy films grown at ~300 C show a well developed band gap with no emission in the region ~0.5 eV below the Fermi level. In comparison with CdTe, which has a band gap of E_g=1.56 eV at room temperature, the alloy film deposited at ~300 C has a much smaller gap.

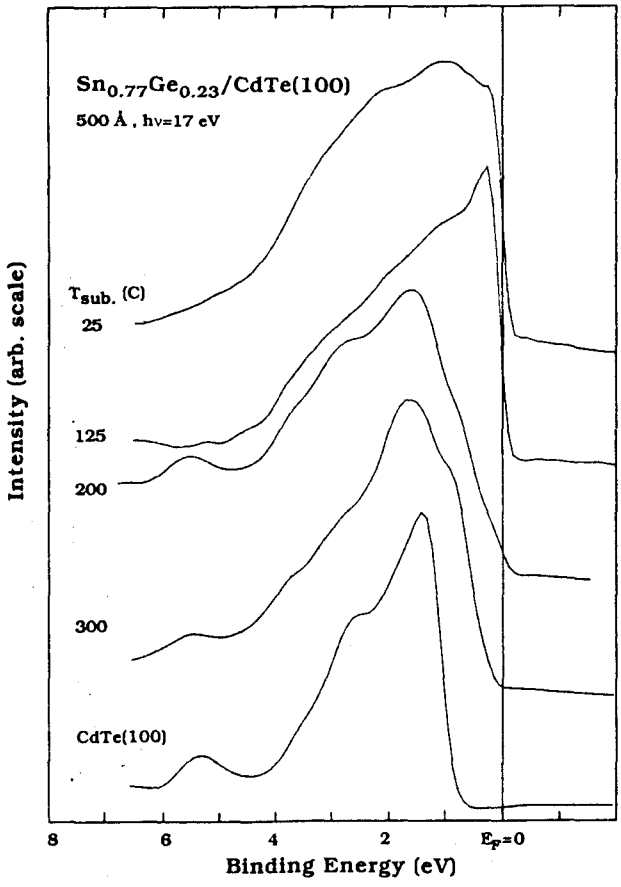

Fig.3: Normal emission valence band spectra of 500 Å $Sn_{0.77}Ge_{0.23}$ grown on CdTe(100) at different substrate temperatures.

Based on Sn4d, Ge3p and Cd4d core level spectra we found a relatively sharp and nonreactive substrate/overlayer interface for deposition temperatures $T_{sub.}$~150 C. For higher growth temperatures however, we have indications of increased reactivity and/or diffusion across the heterostructure interface. The Cd4d signal, which was completely attenuated after the room temperature growth of an alloy film 500 Å thick , regained ~16% of the intensity of the clean CdTe(100) substrate after the deposition of the same film at $T_{sub.}$=200 C. At $T_{sub.}$=300 C the Cd4d intensity increased even further to ~30% of that of the clean substrate. Compared to the spectrum of clean CdTe the Cd4d emission is shifted ~0.35 eV towards a higher binding energy for samples grown at elevated substrate temperatures. Additional core level measurements as a function of overlayer thickness indicate that the Cd4d emission originates from a $Cd_{1-x}Sn_xTe$ compound formed at $T_{sub.}$~200-300 C.

The formation of an additional Sn- compound is also obvious from Fig.4 which shows the evolution of the Sn4d spectra at different substrate temperatures. Compared to an α-Sn sample the Sn/Ge alloy shows a small energy shift which is characteristic of the metallic β-phase. Deposition at ~200 C leads to a second Sn4d doublet which is shifted ~0.8 eV towards higher binding energies. At $T_{sub.}$=300 C the the reaction is completed and the spectrum consists of only one chemically shifted Sn4d doublet.

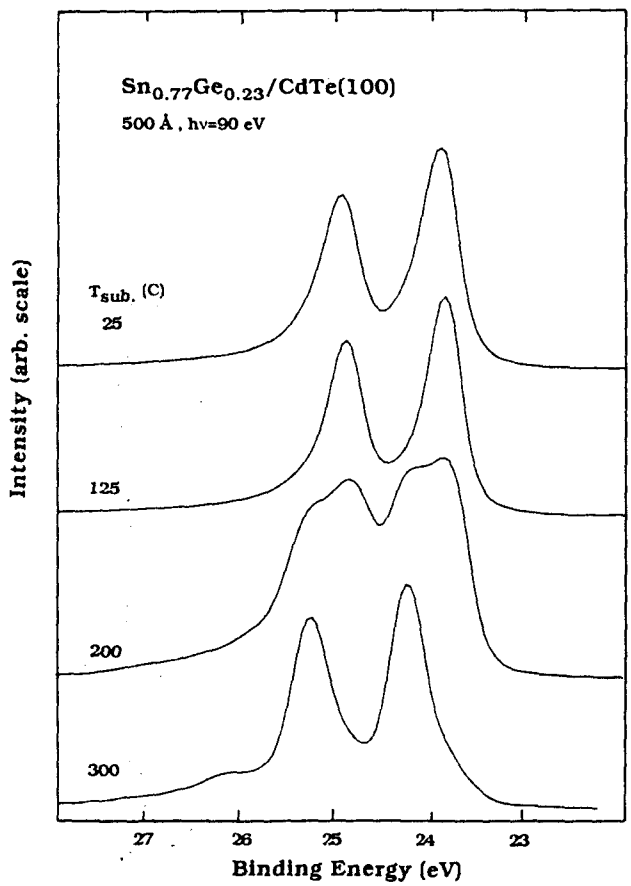

Fig.4: Sn4d core spectra of 500 Å $Sn_{0.77}Ge_{0.23}$ grown on CdTe(100) at different temperatures

Our growth studies indicate that it is not possible to grow thick homogeneous epitaxial films of α-Sn_xGe_{1-x} alloys on CdTe (100) substrates. Good layer by layer epitaxy is limited by insufficient surface mobilities at growth temperatures below ~150 C to a thickness <100 Å. At higher substrate temperatures increased reactivity with the CdTe substrate prevents the formation of an abrupt smooth epilayer.

Germanium is less reactive than CdTe and permits the alloy deposition at higher substrate temperatures. Growth studies showed that metastable Sn/Ge alloys can be manufactured by MBE at temperatures ~400 C. homogeneous films with reasonable crystalline quality were grown up to ~300Å on Ge(100) substrates. Even though the temperature for epilayer growth is ~400 C we could not find the precipitation of significant amounts of the metallic β-phase for depositions at lower temperatures. RHEED, as well as core and valence band photoemission spectra, instead indicated the growth of an amorphous alloy for $T_{sub.}$<200 C.

In comparison with clean Ge(100), angle resolved valence band spectra of α-Sn/Ge show only small changes of the deeper valence band structure. However, differences of the alloy electronic structure are present at the region close to the top of the valence band maximum as can be seen from Fig.5. A comparison with the spectra of clean Ge (dashed lines) clearly shows the additional alloy emission in the gap region. For hν=20 eV the top of the valence band emission develops a pronounced shoulder ~0.16 eV below the Fermi level E_F. A more detailed discussion of the origin of the spectral features and their relationship to the electronic band structure is given elsewhere[11]. The important experimental information can be summarized as follows: the dispersion of lower lying valence bands of α-Sn_xGe_{1-x} alloys follows very closely that of Ge for k values along the ΓX direction.

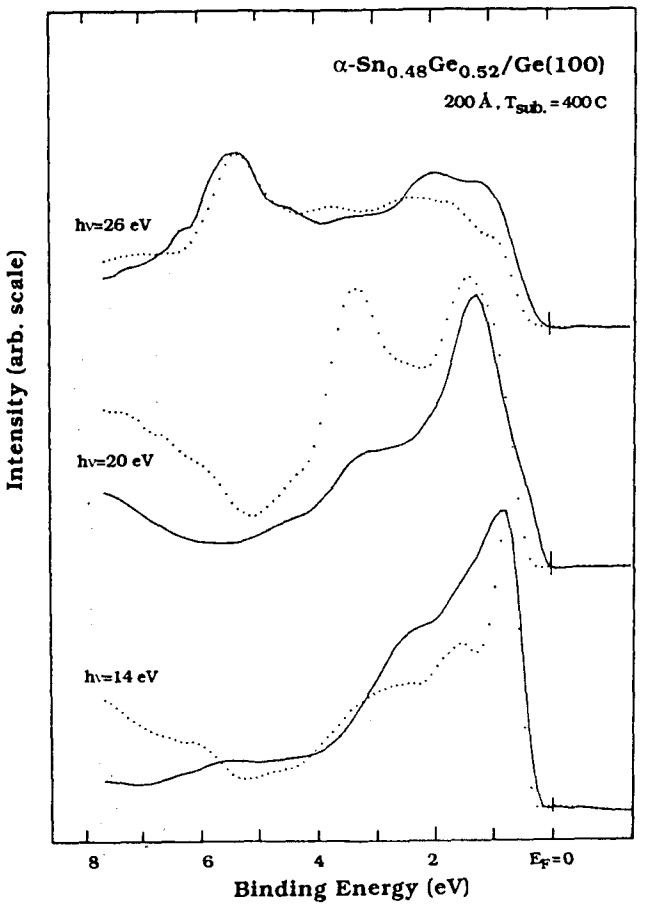

Fig.5: Normal emission valence band spectra of α-$Sn_{0.48}Ge_{0.52}$ grown at 400 C on Ge(100). The corresponding spectra of clean Ge(100) are shown with a dotted line

The Γ_8 emission of the alloy moves from ~0.6 eV for Ge(100) to ~0.16 eV below E_F. The observed shift is caused by an upward motion of the Γ_8 valence band indicating the narrowing of the band gap with increasing amounts of Sn. Core level measurements do not show the same energy shift between Ge and the alloy and thus rule out the possibility that Fermi level motion could be the cause of the observed shift of the Γ_8 point between both materials.

Finally we would like to mention that we observed a strong tendency to form an alloy with a composition close to x~0.5. Presently we are not able to determine if the alloy composition is homogeneous throughout the entire film or if it is a phenomena related to surface segregation. However, the compositional pinning effect is not unusual and has been seen previously for the coherent growth of several disordered alloys[12,13]. Recent first principle total energy calculations were able to confirm the observed stability of ordered epitaxial $GaAs_xSb_{1-x}$ films at growth temperatures well below the miscibility- gap temperature[14].

III. Conclusions

The deposition of α-Sn_xGe_{1-x} alloys on CdTe(100) at $T_{sub.}$<150 C results in a three dimensional cluster growth with considerable amounts of precipitated metallic β-Sn. For higher substrate temperatures we find increased interfacial reactivity with CdTe which prevents the growth of a homogeneous single phase alloy film.

Alloy films of good crystalline order can be grown at $T_{sub.}$~400 C on Ge(100) substrates up to a

thickness of ~200-300 Å. Photoemission core level measurements indicate a preferred growth of the alloy with x~0.5.

Angle resolved valence band spectra provide evidence of the expected closing of the band gap by alloying Sn with Ge. For an alloy with x~0.48 we found a shift of the Γ_8 valence band maximum to ~0.16 eV below E_F. Assuming a linear model the band gap for an alloy with x~0.48 would be E_g~0.2 eV which places the bottom of the Γ_7 conduction band ~0.04 eV above E_F.

Additional growth studies of α-Sn_xGe_{1-x} alloy films on lattice matched substrates *eg* GaSb(100) and ZnTe(100) are under investigation and results will be reported elsewhere[15].

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V. References

* present address: Max Planck Institut für Festkörperforschung, 7000 Stuttgart 80 FRG

1. S. Oguz, W. Paul, T.F. Deutsch,B-Y. Tsaur, and D.V. Murphy, Appl.Phys. Lett. **43**, 848 (1983).
2. D. W. Jenkins, and J. D. Dow, Phys. Rev. B **36**, 7994 (1987).
3. G. A. Busch and A. Kern, *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic Press, New York, 1961), Vol. 11 , p. 1.
4. T. Soma, H. Matsuo, and S. Kagaya, phys. stat. sol. (b) **105**, 311 (1981).
5. J. Menendez, and H. Höchst, Thin Solid Films. **111**, 375 (1984).
6. H. Höchst, D. W. Niles, and I. Hernández-Calderón, J. Vac. Sci. Technol. B **6**, 1219 (1988) and references therein
7. C. A. Hoffman, J. R. Meyer, F. J. Bartoli, M. A. Engelhardt, and H. Höchst, to be publ.
8. J. C. Bean , J. Vac. Sci. Technol. **B4** , 1427 (1986) and references therein.
9. A. Kobabayashi, S. M. Paik, and S. D. Sarma, J. Vac. Sci. Technol. **B6** , 1145 (1988).
10. H. Höchst and I. Hernández-Calderón, J. Vac. Sci. Technol. A **3**, 911 (1985).
11. H. Höchst, M. A. Engelhardt, and I. Hernández-Calderón , to be publ.
12 R. F. C. Farrow, J. Vac. Sci. Technol. B **1**, 222 (1983
13. M. J. Jou, Y. T. Cherng, H. R. Jen, and G. B. Stringfellow, Appl. Phys. Lett. **52**, 549 (1988)
14. D. M. Wood, and A. Zunger, Phys. Rev. B **38**, 12756 (1988).
15. M. A. Engelhardt , and H. Höchst, to be publ.