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TERTIARYBUTYLDIMETHYLANTIMONY FOR InSb GROWTH

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Tertiarybutyldimethylantimony for InSb Growth

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Abstract

Trimethylantimony (TMSb) is the standard Sb source for OMVPE growth of Sb-containing materials. However, TMSb pyrolyzes slowly for temperatures below 500 °C, limiting its usefulness for low temperature growth. Recently, triisopropylantimony (TIPSb) has successfully been used to grow InSb. This allows the growth of high quality layers at V/III ratios near unity for temperatures as low as 430 °C. For lower temperatures, higher V/III ratios are required due to incomplete TIPSb pyrolysis. This causes problems for the small bandgap materials which require growth temperatures lower than 400 °C. In this work, tertiarybutyldimethylantimony (TBDMSb) was used, together with trimethylindium (TMIn), for the growth of InSb. The optimum V/III ratio is near unity for growth temperatures from 375 to 450 °C. Good surface morphology InSb layers can also be obtained at temperatures as low as 350 and 325 °C at moderate V/III ratios of 10 and 17, respectively. Using this new Sb source, the growth temperature can be reduced by more than 100 °C as compared to TMSb, and about 50 °C as compared to TIPSb. Another advantage of using TBDMSb is that the surface morphology for InSb grown using TBDMSb does not depend on V/III ratio as critically as for InSb grown using TIPSb. Moreover, the growth efficiency is high, on the order of 1×10^4 µm/mole, for temperatures higher than 400 °C. This indicates that there are minimal parasitic reactions between TMIn and TBDMSb. The electron concentration is near 10^{16} cm^{-3} for growth temperatures of between 450 °C and 375 °C. It increases slightly to ~10^{17} cm^{-3} for T_g=350 and 325 °C. The 10 K photoluminescence spectra show well-resolved peaks due to exciton and impurity recombination. Samples grown at temperatures higher than 400 °C exhibit higher PL intensities than those grown at lower temperatures. The results indicate that TBDMSb is an excellent replacement for TMSb and TIPSb for the growth of InSb.

1. INTRODUCTION

The conventional Sb-containing alloys have energy bandgaps as low as 150meV (8 μm) [1]. They are important materials for infrared applications. Recently, Bi has been successfully used in order to further lower the energy bandgap to the 12 μm range [2, 3]. Bi concentrations of greater than 6% have been obtained for InAsBi alloys [3], with a reported reduction in energy bandgap at a rate of 55 meV per percent Bi [2]. Samples with higher Bi concentrations require growth temperatures as low as 275 °C [3]. At this low temperature, the conventional Sb source [4, 5], trimethylantimony (TMSb), decomposes very slowly [6]. Thus, other Sb sources are needed for the low temperature growth of alloys such as InAsSbBi.

Recently, we have investigated trivinylantimony (TVSb, $(C_2H_3)_3Sb$) [7], triisopropylantimony (TIPSb, $(C_3H_7)_3Sb$) [8], and triallylantimony (TASb, $(C_3H_5)_3Sb$) [8] as possible substitutes for TMSb. For TVSb, the value of T_{50} (temperature for 50% decomposition) in He is actually slightly higher than for TMSb [6, 7], limiting its usefulness. On the other hand, TASb is too labile: It decomposes slowly during storage at room temperature [9]. To date, only TIPSb has been successfully used to grow InSb at temperatures as low as 300 °C [10, 11].

In this work, we report the use of the newly-developed Sb source, tertiarybutyldimethylantimony (TBDMSb), as a replacement for TMSb for the OMVPE growth of InSb.

2. Experimental

The freezing point of TBDMSb is approximately 8 °C and its boiling point is 56 °C. The vapor pressure of TBDMSb has been measured to be 4.5 torr at 12 °C, 7.3 torr at 23 °C, 8.1 torr at 26 °C, 45 torr at 56 °C, and 53 torr at 63 °C. The best fit for these data yields

$$\log P\ (\text{torr}) = 8.0932 - \frac{2132.4}{T(K)} \quad ,$$

giving a vapor pressure of 7.7 torr at 23 °C. This value is much higher than the 0.5 torr for TIPSb at the same temperature [10]. Thus, TBDMSb is more convenient to use than TIPSb. The decomposition of TBDMSb has been studied in an isothermal flow tube reactor with a residence time of approximately 3.2 seconds at 300 °C [12]. The value of T_{50} (the temperature for 50% decomposition) is 300 °C in both He and D_2 ambients. In contrast, the values of T_{50} for TMSb are approximately 510 and 440 °C in He and D_2, respectively [6]. Thus, lower growth temperatures may be possible when TBDMSb is used.

The epilayers were grown in an atmospheric pressure, horizontal OMVPE reactor. The cross section of the rectangular quartz reactor tube is 5 cm wide and 2 cm high. The carrier gas for the liquid and/or solid sources was palladium-diffused hydrogen, with a total flow rate of ~1200 cc/min. Separate stainless steel tubing was used for the group III and group V reactants in order to minimize possible parasitic reactions [13]. The mixing of the group III and V reactants occurred immediately before entering the quartz reactor. The In source was trimethylindium (TMIn), obtained from CVD incorporated. Typical flow rates were 150 cc/min for TMIn held at 0 °C and 2.5-100 cc/min for

TBDMSb held at 22 °C. The substrates were undoped (100) InSb and semi-insulating (100) InP.

The surface morphologies were observed using a differential interference contrast microscope. The electrical properties of epilayers grown on semi-insulating InP substrates were characterized using the van der Pauw technique. The measurements were carried out at 77 K to eliminate the contribution of intrinsic carriers. The In contacts on the four corners of the rectangular samples were annealed at 300 °C for 90 seconds under a N_2 ambient. The magnetic field was 5 kG and the sample current was between 10 and 100 μA, depending upon the resistivity of the sample.

Samples for photoluminescence measurements were cooled to 10 K on the cold finger of a closed-cycle He refrigerator. The PL was excited with the 488nm line of an argon laser and detected at the exit slit of a 0.5m spectrometer with a liquid nitrogen cooled HgCdTe photoconductive detector. Conventional lock-in techniques were used to amplify the signal.

3. Results and Discussion

The surface morphologies of InSb layers grown on InSb substrates at 450 and 425 °C are shown in Fig.1 for several values of input V/III ratio. For a growth temperature of 450 °C, In-droplets are clearly seen on the surface for the sample grown at a V/III ratio of 0.33. With an increase in V/III ratio to 0.66, the surface becomes very smooth. Further increases in V/III ratio to 1.3 and 2.0 result in the formation of Sb-hillocks on the surfaces. Similar changes in surface morphology with V/III ratio were also observed for other growth temperatures. For a growth temperature of 425 °C, as shown in the bottom row of Fig.1, the surface changes from an In-rich morphology for a V/III ratio of 0.7 to an Sb-rich morphology at a V/III ratio of 2.8. Fig.2 shows the V/III ratio dependence of surface morphology for growth temperatures of 375 and 350 °C. At 375 °C, the sample grown at a V/III ratio of 1.1 is covered with In-droplets. In fact, many In-droplets have coalesced. The density of the In-droplets is greatly reduced for the sample grown at a V/III ratio of 2.3. The surface becomes very smooth for the sample grown at V/III=3.5. For V/III=4.6, Sb-hillocks are formed on the surface. For samples grown at 350 °C, the surfaces are In-rich for input V/III ratios of 4.7, 5.5, and 10. The morphology becomes Sb-rich at V/III=17, with the appearance of the typical Sb-hillocks. The origin of the dumbbell-shaped hillocks is not clear at this time. It is interesting to note that most In-rich surface morphologies are somewhat shiny since the areas between the droplets are quite smooth.

Figs.1 and 2 show that only a narrow range of V/III ratio can be used for obtaining good surface morphology layers. A low V/III ratio produces In-rich droplets on the surface and a high V/III ratio results in the formation of Sb-hillocks. This limit is not related to the use of TBDMSb, but to the low vapor pressures of both metallic In and Sb, as has been discussed in detail in Ref. [14]. For samples grown at low V/III ratios, the excess In forms a liquid phase on the surface, leading to vapor-liquid-solid (VLS) three-phase growth [15, 16]. The whiskers are difficult to see from the top view in Figs.1 and 2, but they can be readily seen when the samples are examined in the cross-sectional view. For samples grown using high V/III ratios, the excess Sb also forms a second phase. However, since Sb has a melting point of 630 °C, VLS growth does not occur. Instead, the excess Sb forms a second solid phase which facilitates the growth of hillocks.

Fig.3 summarizes the V/III dependence of surface morphology observed in Figs.1 and 2 and those reported earlier for a growth temperature of 400 °C [17]. For comparison, Fig.3 also shows the optimum V/III ratio versus temperature for InSb grown using TIPSb and TMIn in the same reactor [10]. It is seen from Fig.3 that the optimum V/III ratio is approximately unity for InSb grown at 450 °C. This is not surprising because both TMIn and TBDMSb are expected to be completely decomposed [12, 18]. As the growth temperature is decreased, the optimum V/III ratio increases. This indicates that TBDMSb is not completely decomposed for temperatures lower than about 370 °C. This temperature is somewhat higher than that reported previously for TBDMSb decomposition [12]. The difference is due to factors such as residence time in the hot zone and temperature profiles, as discussed in detail in Ref. [10].

Fig.3 shows that the growth temperature can be reduced by about 50 °C when TIPSb is replaced with TBDMSb. For example, using TBDMSb, InSb can be grown using low V/III ratios of 2.4 and 3.5 at 400 and 375 °C, respectively. Even at 350 °C, the V/III ratio is still a moderate value of about 15. In contrast, the surface morphology is routinely rough for layers grown using TIPSb at temperatures lower than 400 °C with V/III ratios of about 20 in the same reactor [10]. Thus, TBDMSb is superior to TIPSb for low temperature growth. Stauf et al [11] have also reported the growth of InSb using TIPSb, but it is difficult to compare their results with the present work since the reactor geometries are quite different. This can lead to significantly different decomposition temperatures for a precursor [10].

The only difference between this study and that reported in Ref.11 is that the total flow rate in this study is about half of that for InSb growth using TIPSb.

This is done to enhance the percentage decomposition of TMIn at low temperatures where TMIn decomposition is slow, resulting in low growth rates, as discussed below. Of course, the lower total flow rate can also enhance the TBDMSb percent decomposition. However, the increase in percent decomposition for TMIn and TBDMSb tend to cancel out, leaving the optimum V/III almost unchanged. In fact, InSb layers have been grown at 375 °C using the same total flow rate as used in Ref [10]. It is found that the layer is In-rich at V/III=1.6 and Sb-rich at V/III=4.6 and near optimum for V/III=3.5. This result is comparable to that shown in Fig. 3. This confirms that TBDMSb is superior to TIPSb for low temperature growth.

It is somewhat unexpected that TBDMSb can be used at lower growth temperatures than for TIPSb since the T_{50} values for TIPSb and TBDMSb decomposition have been reported to be nearly the same in an ersatz reactor under the same conditions [12]. However, differences exist between the ersatz and growth reactors, yielding different decomposition behavior for precursors in the two reactors. For example, the T_{50} value has been reported to be about 325 °C for TMIn [18] and about 300 °C for TIPSb [8] in the ersatz reactor under identical conditions. However, TIPSb apparently decomposes more slowly than TMIn in the OMVPE growth reactor [10], as seen from the V/III ratio dependence of InSb surface morphology as well as from studies of the separate decomposition of In and Sb on a substrate. Such differences are partially due to differences in the ratios of homogeneous and heterogeneous reactions in the two types of reactors. In the ersatz reactor, TIPSb and TBDMSb decompose homogeneously [8, 12]. In the OMVPE growth reactor, heterogeneous reactions may play a much more important role, since the hot zone is confined to a thin boundary layer. This is especially true at low temperatures where heterogeneous decomposition generally dominates. In addition to differences in the temperature profile, the surfaces in the two reactors are different. The surface is either In or Sb metal in the ersatz reactor, while the surface is InSb in the deposition area of an OMVPE growth reactor. This could lead to different heterogeneous decomposition rates in the two reactors.

Fig.4 shows the V/III ratio dependence of growth efficiency for InSb grown using TMIn and TBDMSb at different temperatures. The growth efficiency is defined as growth rate divided by the group III molar flow rate [19]. The growth efficiency is near 10^4 μm/mole for growth temperatures of ≥400 °C. The high value of growth efficiency is comparable to results for the growth of other materials in the same reactor using more conventional sources. The results indicate that there is mimimal parasitic reaction between TMIn and TBDMSb. For lower temperature growth, the growth efficiency decreases because TMIn is not completely decomposed [3]. The V/III ratio dependence of growth efficiency generally shows that the growth efficiency increases as the V/III ratio increases under the In-rich conditions and does not depend on the V/III ratio under the Sb-rich conditions. This trend is especially clear for the 375 and 350 °C data where the change in V/III ratio is large. In the In-rich region, whiskers are formed as discussed earlier and shown in Fig.3(a). The growth of whiskers leads to less In available for the growth of InSb. Thus, lower V/III ratios produce more whiskers, resulting in the smaller "apparent" growth efficiency. In the Sb-rich regions, the excess Sb does not lead to whisker growth. Thus, the growth efficiency shows no dependence on V/III ratio. This is well known for the growth of GaAs and other similar materials [20].

The 77 K electron concentration is shown in Fig.5 as a function of growth temperature. In general, the lowest electron concentration for InSb at each temperature corresponds to a sample grown at near-optimum conditions. The background electron concentration is in the range of 10^{16} cm^{-3} for temperatures between 450 and 375 °C. It increases slightly to ~10^{17} cm^{-3} for growth temperatures of 350 and 325 °C. The increase in electron concentration is much less than that for InAs grown using TMIn and AsH_3 [2, 3], also shown in Fig.5 for comparison. For InAs growth, the electron concentration increased to approximately 10^{19} cm^{-3} at 325 °C. The donor impurity in InAs has been identified as carbon using Secondary Ion Mass Spectrometry (SIMS) [2, 3]. The incorporation of carbon as a donor has been attributed to the relative strengths of the As-CH_3 and In-CH_4 bonds [2, 3, 21]. The carbon in InSb is also expected to be a donor since the Sb-CH_3 bond is stronger than the In-CH_3 bond [21]. However, the Sb-CH_3 bond is weaker than the As-CH_3 bond [21]. This argument suggests that less carbon would be incorporated into InSb than into InAs. Although the donor impurity in InSb grown using TBDMSb has not been identified, the results in Fig.5 show that the carbon incorporation for InSb grown using TMIn and TBDMSb is indeed much less than that for InAs grown using TMIn and AsH_3. Thus, carbon incorporation does not appear to be a major problem. Similar result has been reported for InSb layers grown at 300-350 °C using TIPSb and TMIn [11], consistent with the above argument that less carbon is incorporated due to the relative bond strengths of Sb-C and As-C.

Fig.6 shows 10K PL spectra as a function of growth temperature. For comparison, a spectrum taken from an InSb substrate is also shown at the bottom of the figure. The spectra exhibit three clearly resolved peaks due to exciton(234meV) and impurity(228 and 213meV) recombination with half-widths comparable to that of the substrate. As expected, reducing the growth temperature resulted in a decrease in PL intensity. It was also observed that the relative intensity of the shallow impurity peak increases as the temperature decreases, suggesting a higher impurity concentration in samples grown at lower temperatures, although the 350 °C spectrum does not follow this trend and is also seen to be shifted to slightly lower energy. This behavior is attributed to the fact that the excitation intensity had to be increased by a factor of three in order for the spectrum to be measured. This led to the dominance of the exciton peak and to some heating of the sample, resulting in the shift to lower energy. The V/III ratio dependence of the PL has also been measured. In general, the V/III ratio has only a small effect on the three main peaks and the best quality material is obtained for V/III ratios of close to unity, the V/III ratio for optimum surface morphology, as seen in Fig.3.

4. Conclusions

In summary, TBDMSb has been successfully used to grow good surface morphology InSb epilayers at temperatures between 450 and 325 °C. The growth temperature can be reduced by more than 100 °C as compared to using TMSb, and by about 50 °C as compared to using TIPSb. The growth efficiency of InSb is about 10^4 μm/mole at high temperatures, indicating minimal parasitic reactions between TMIn and TBDMSb. The as-grown epilayers have background electron concentrations on the order of 10^{16} cm^{-3} for temperatures near 425 °C, increasing to 10^{17} cm^{-3} for temperatures of 350 and 325 °C. Low temperature PL spectra show well resolved and narrow exciton and impurity peaks that are similar to those of an InSb substrate. The results show that TBDMSb is an excellent replacement for TMSb for low temperature growth.

5. Acknowledgements

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6. References

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Figure Captions:

Fig.1 V/III ratio dependence of surface morphology for InSb grown using TBDMSb and TMIn at 450 and 425 °C.

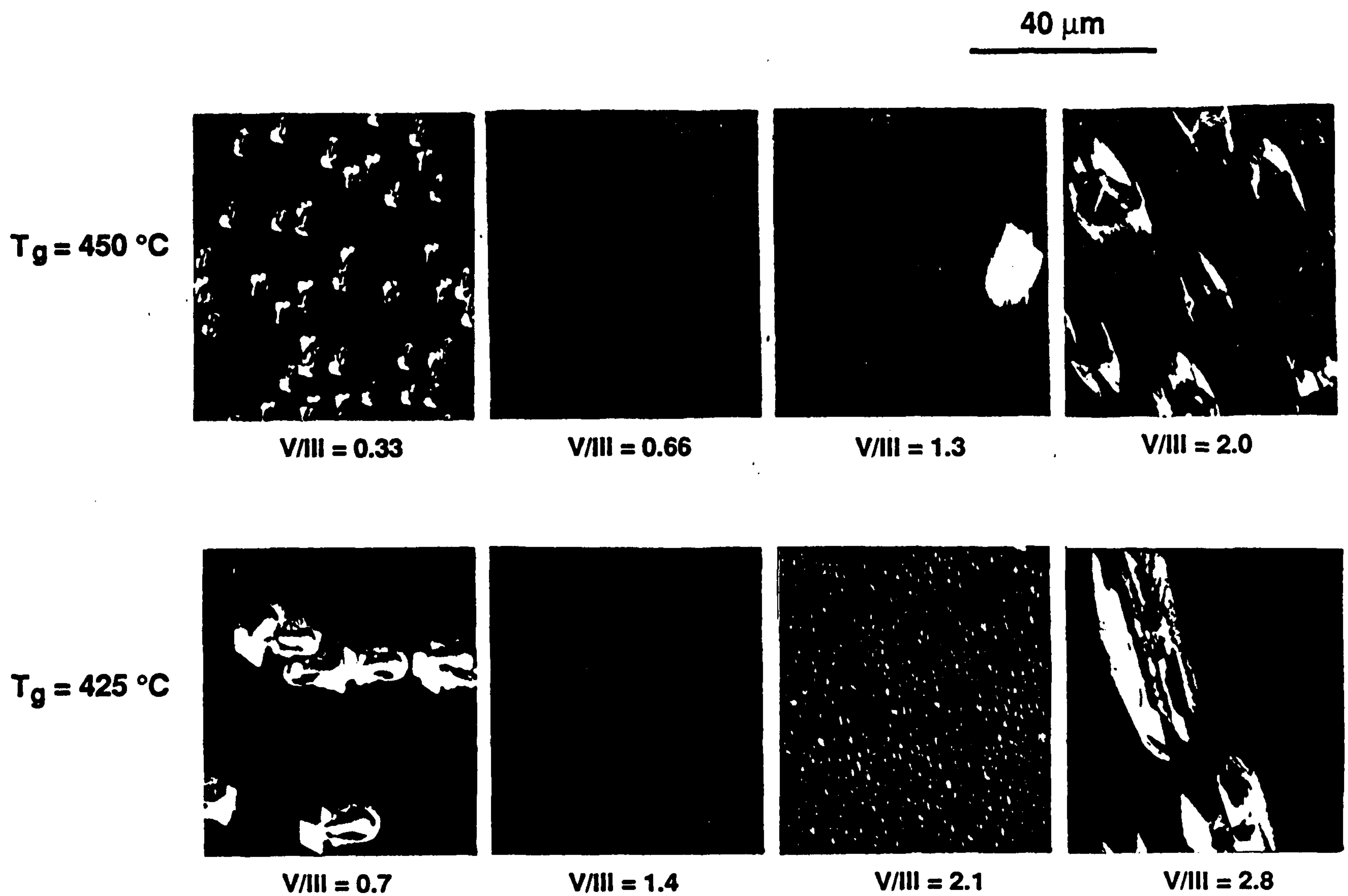
Fig.2 V/III ratio dependence of surface morphology for InSb grown using TBDMSb and TMIn at 375 and 350 °C.

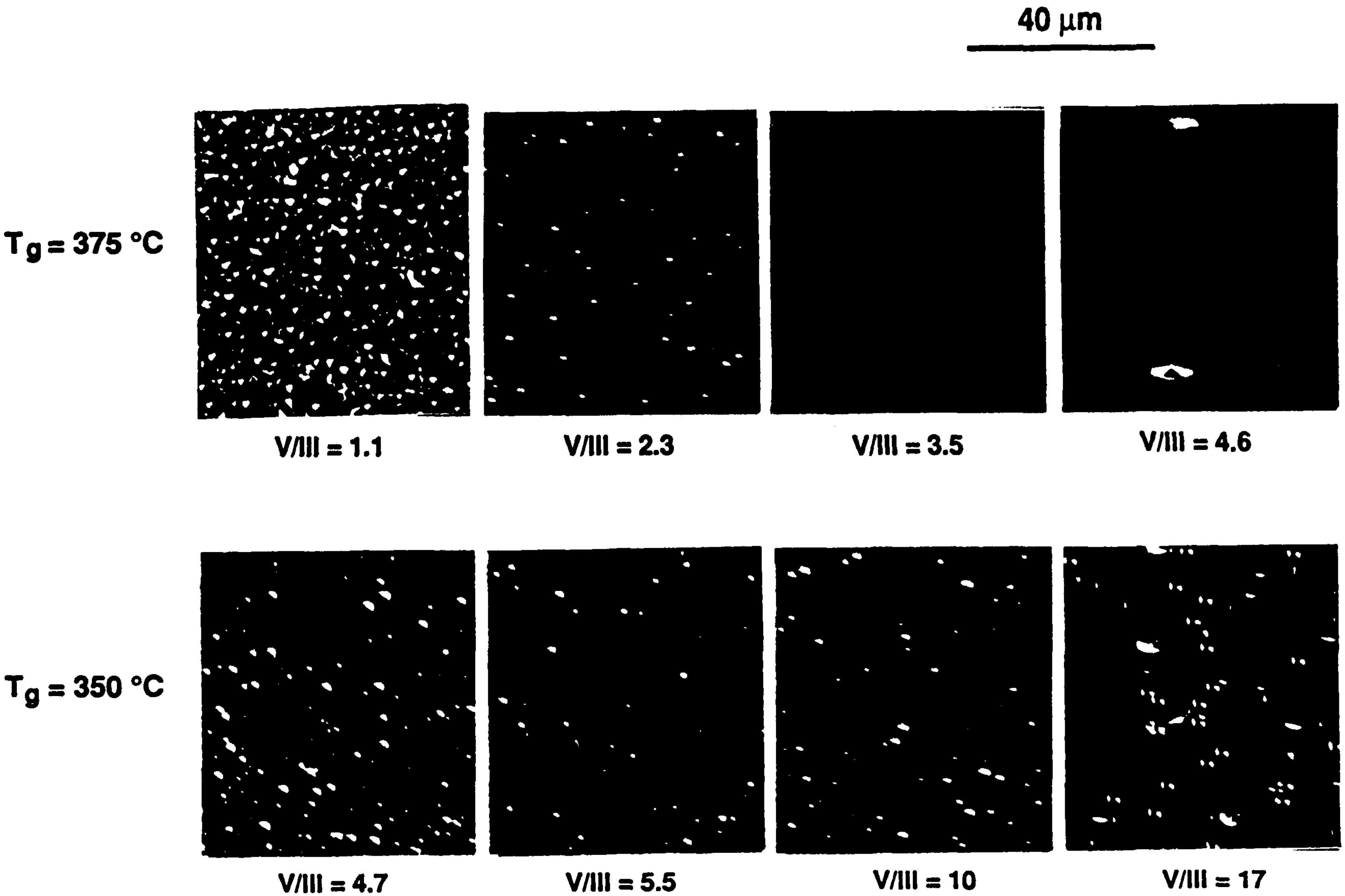
Fig.3 Summary of InSb surface morphology as a function of temperature and V/III ratio. For comparision, the results for InSb grown using TIPSb and TMIn is also shown [11].

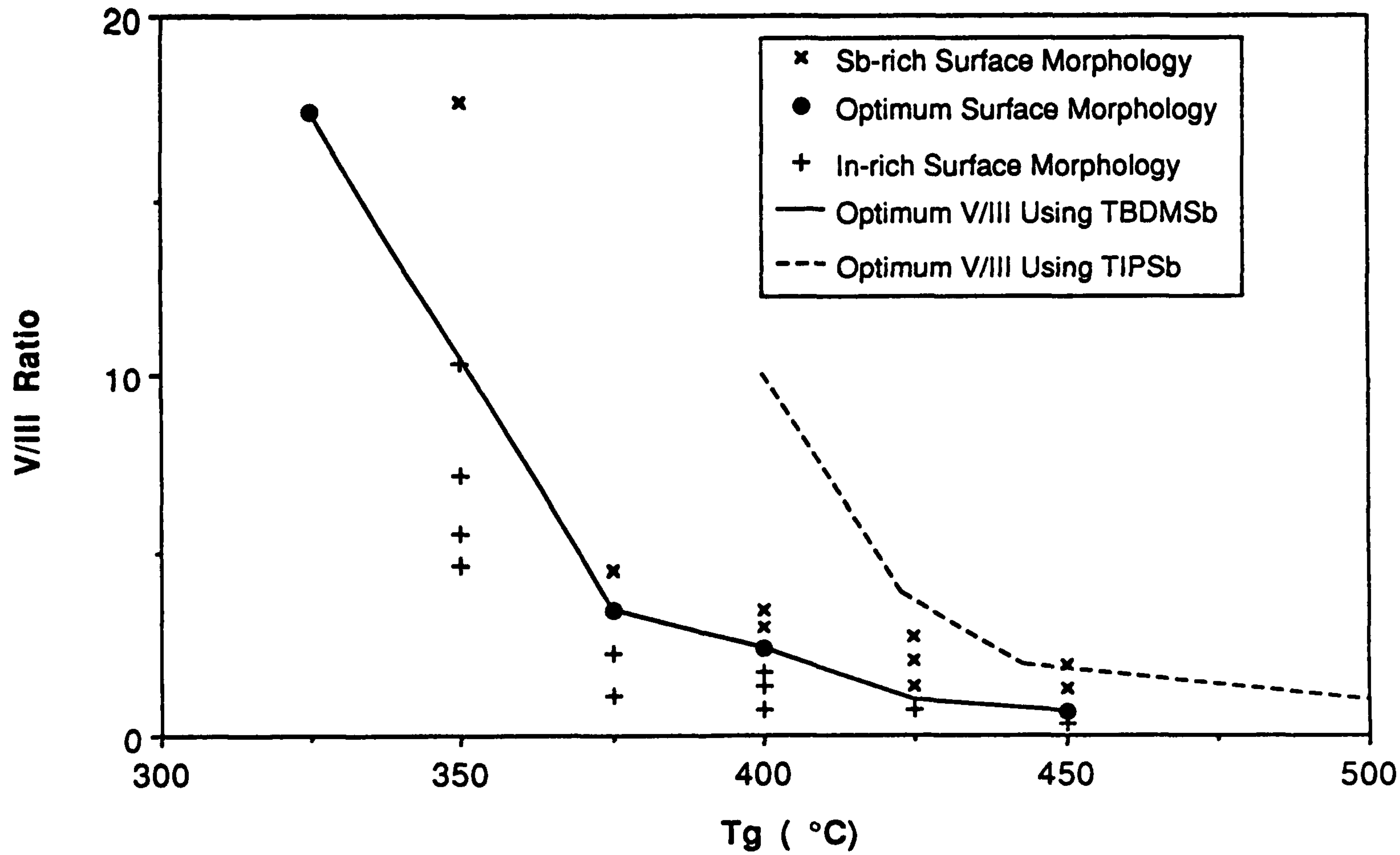
Fig.4 InSb growth efficiency as a function of V/III at several temperatures.

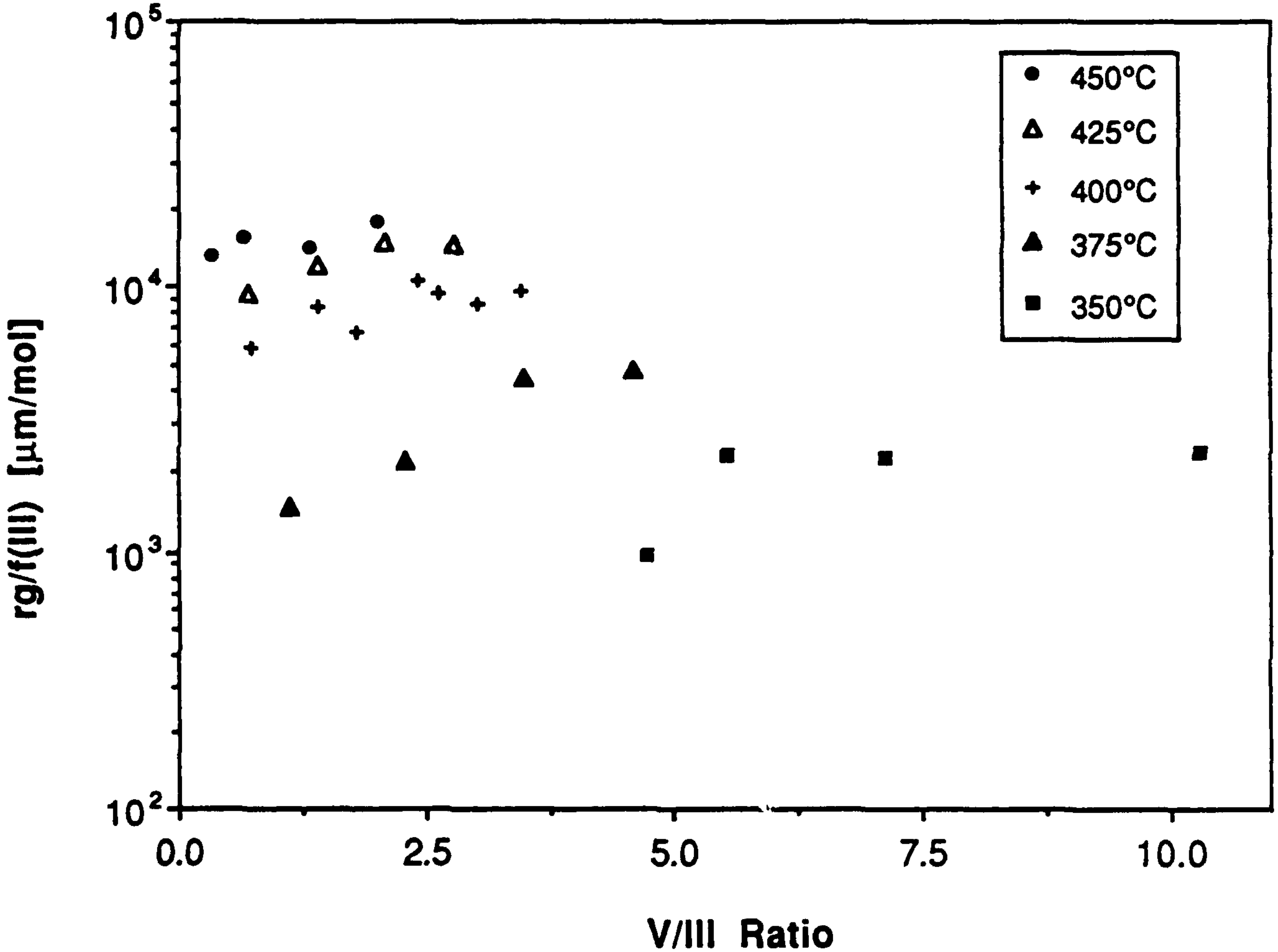
Fig.5 The 77 K electron concentration versus growth temperature for InSb grown using TBDMSb and TMIn. The electron concentration for InAs grown using TMIn and AsH_3 is also shown for comparison [2, 3]

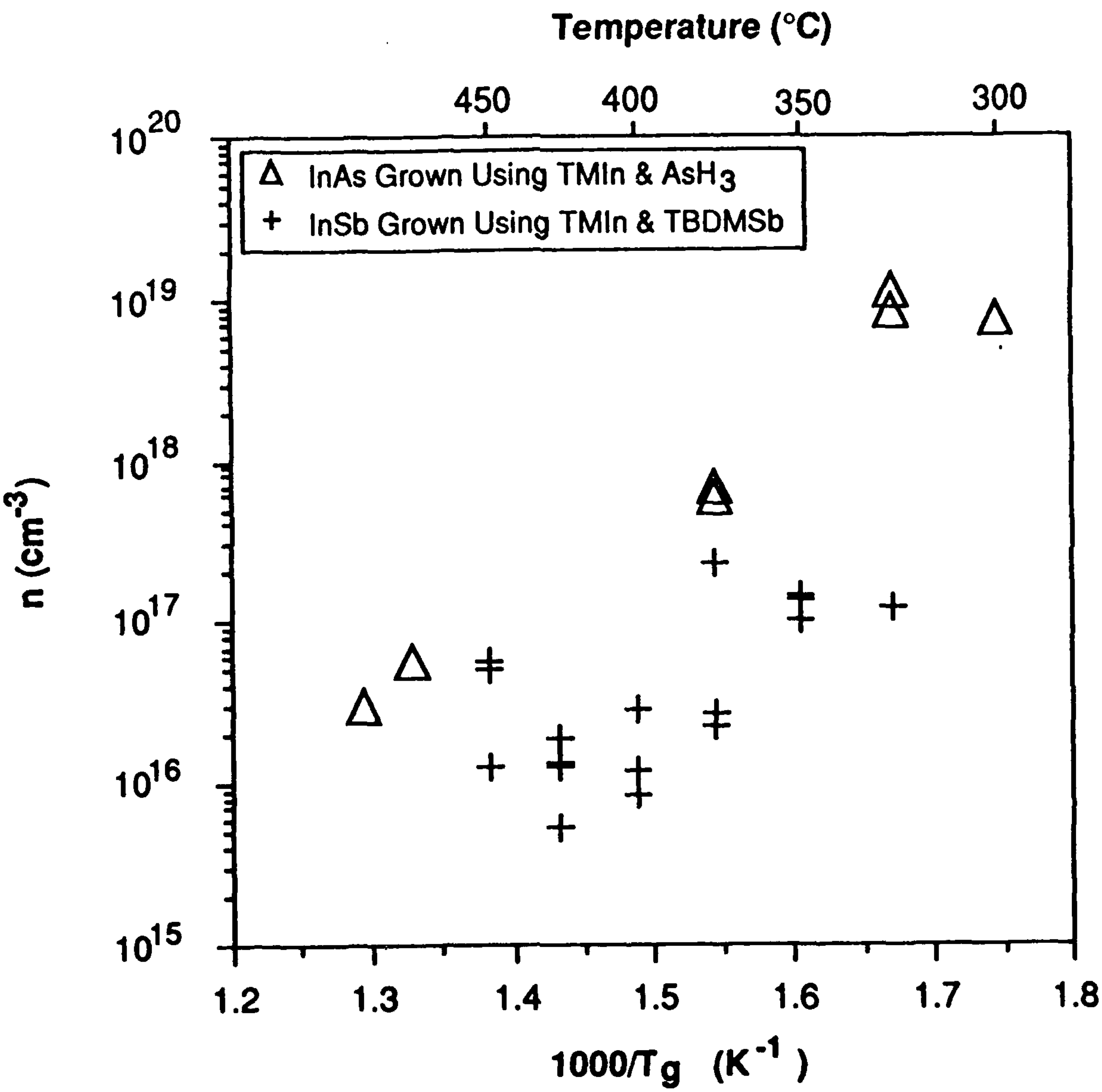
Fig.6 Low temperature PL spectra for samples grown at different temperatures.


40 μm
Tg = 450 °C
Tg = 425 °C
V/III = 0.33
V/III = 0.66
V/III = 1.3
V/III = 2.0
V/III = 0.7
V/III = 1.4
V/III = 2.1
V/III = 2.8

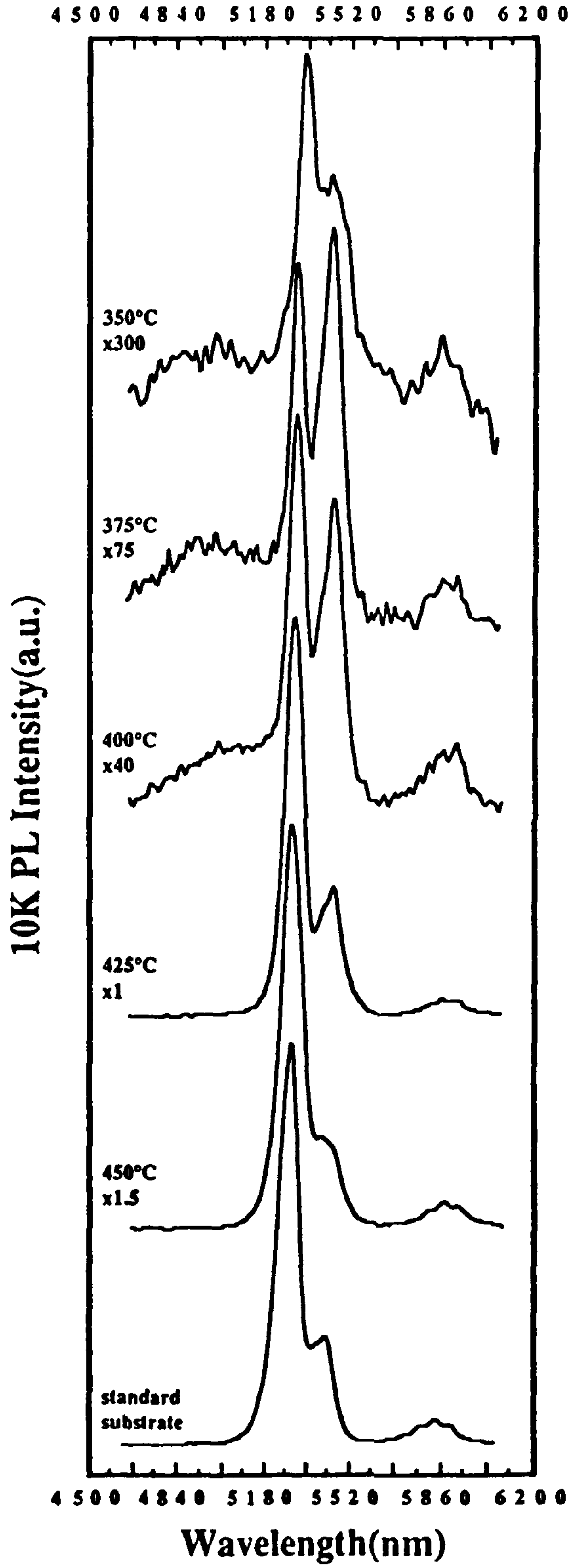

40 μm
Tg = 375 °C
V/III = 1.1
V/III = 2.3
V/III = 3.5
V/III = 4.6
Tg = 350 °C
V/III = 4.7
V/III = 5.5
V/III = 10
V/III = 17


Sb-rich Surface Morphology
Optimum Surface Morphology
In-rich Surface Morphology
Optimum V/III Using TBDMSb
Optimum V/III Using TIPSb
V/III Ratio
0
10
20
300
350
400
450
500
Tg (°C)


450°C
425°C
400°C
375°C
350°C
10^5
10^4
10^3
10^2
rg/f(III) [µm/mol]
0.0
2.5
5.0
7.5
10.0
V/III Ratio



Temperature (°C)
450
400
350
300
10^{20}
10^{19}
10^{18}
10^{17}
10^{16}
10^{15}
n (cm^{-3})
Δ InAs Grown Using TMIn & AsH_3
+ InSb Grown Using TMIn & TBDMSb
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1000/T_g (K^{-1})



4500 4840 5180 5520 5860 6200
350°C
x300
375°C
x75
400°C
x40
425°C
x1
450°C
x1.5
standard
substrate
10K PL Intensity(a.u.)
4500 4840 5180 5520 5860 6200
Wavelength(nm)