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LPCVD OF InN ON GaAs(110) USING HN_3 AND TMIn: COMPARISON WITH Si(100) RESULTS

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ABSTRACT

Low-pressure chemical vapor deposition (LPCVD) of InN and laser-assisted LPCVD on GaAs(110) and Si(100) using HN_3 and trimethyl indium (TMIn) has been studied with XPS, UPS and SEM. Without 308-nm excimer laser irradiation, InN film was built on the GaAs but not on Si surface under the present low-pressure conditions. When the photon beam was introduced, InN films with In:N atomic ratio of 1.0±0.1 and a thickness of more than 20 Å (the limit of the electron escaping depth for the In_{3d} X-ray photoelectrons) were formed on Si(100) surface. In both cases, the formation of surface nitrides at the initial film growth processes was clearly indicated in the XP spectra. The He(II) UP spectra taken from InN films on GaAs and Si are nearly identical and agree well with the result of a pseudo-potential calculation for the InN valence band. The corresponding SEM pictures showed smooth InN films on GaAs(110), while grains with diameter of ~100 nm were observed for InN on Si(100).

INTRODUCTION

The growth of III-V nitride semiconductor materials has been the subject of intense interest in the past decade. Because of their wide direct band-gaps, these materials have a potential for use in electronic and optoelectronic devices such as visible-light semiconductor lasers, ultraviolet light detectors and laser diodes. However, few articles have been published regarding the growth InN crystals or thin films, probably because InN has a low dissociation temperature and thus low-temperature growth is required [1,2].

Recently it has been shown that the CVD of InN and InGaN on sapphire substrates can be achieved by using TMIn, TEGa and NH_3 under extremely high V/III ratios (>10^4) [3]. Other methods, such as reactive rf-sputtering and ion plating have been used in an effort to produce InN films [4-7]. Using low energy In^+ and N_2^+ ion beams, Bello et al. [8] were able to grow InN on a Si(100) surface; however, the resulting InN showed an N:In atomic ratio of <0.4. In this paper, we report the results of LPCVD of InN on GaAs(110) and Si(100) surfaces using HN_3 and TMIn, aided by 308-nm photon excitation in the latter case.

EXPERIMENTAL

The present experiment was carried out in a custom-designed ultra-high vacuum (UHV) system (Leybold, Inc.) which is composed of two compartments, one for the surface analysis and the other for film deposition as described elsewhere [9,10]. HN_3 and TMIn samples were prepared in the same manner as described in references [11] and [12].

GaAs(110) single crystals from Laser Diode, Inc. were cut into 0.5 cm x 1.5 cm samples. They were cleaned with 5% hydrogen fluoride (HF) solution and then annealed at 1500 K *in vacuo* bombarded with 2.5 keV Ar^+ ion beam followed by annealing at 770 K. TMIn and HN_3 samples were introduced into the system through two separate 1/8" stainless steel tubes, whose ends were ~1/2" above the surface. After a designated deposition time, the sample was moved into the surface analysis chamber for X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) measurements and then moved back to the deposition chamber for continuing film deposition. When the deposition was finished, the samples were taken out of the vacuum chamber and stored in N_2 atmosphere before scanning electron microscopy (SEM) measurements.

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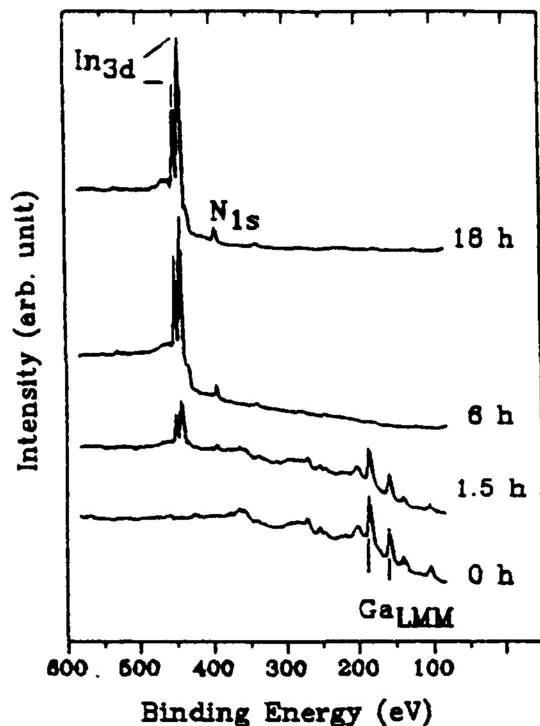

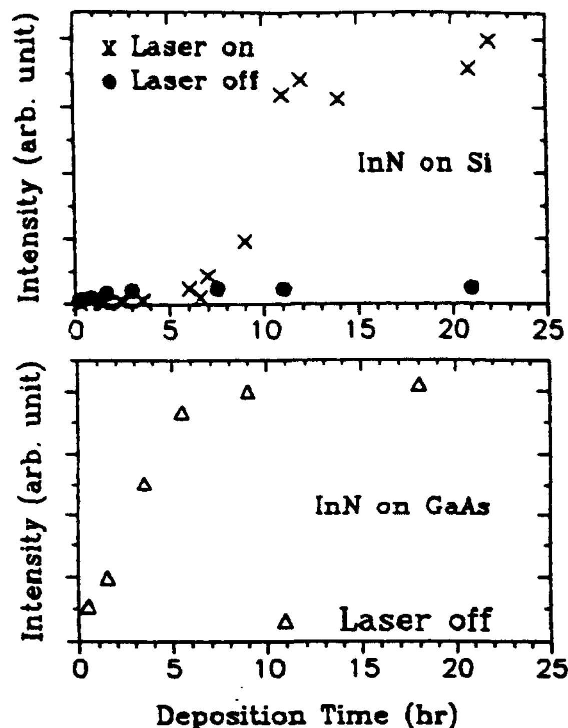

Fig.1 XP spectra for InN on GaAs at the indicated deposition times.

Fig.2 The dependence of $In_{3d\ 5\ 2}$ XPS signal intensity on InN deposition time.

RESULTS

Figure 1 shows XP spectra taken from a clean GaAs(110) and after InN deposition for 1.5, 6 and 18 h. The deposition was carried out at $P_{TMIn} = 2x10^{-7}$, $P_{HN3} = 1x10^{-6}$ torr and $T_s = 700$ K. For the clean surface, XPS showed major peaks at 204, 140, 104, 189 and 162 eV due to $As_{3d-1/2}$, $As_{3p-3/2}$, Ga_{3p} photoelectrons and Ga_{LMM} and Ga_{LMM} Auger electrons, respectively. These peak intensities decreased continuously as the InN deposition proceeded. Meanwhile, new peaks at 452, 444.4 and 396.6 eV for $In_{3d-3/2}$, $In_{3d-5/2}$, and N_{1S} photoelectrons increased and dominated the spectra after a deposition of ≥6 h.

Figure 2 compares the $In_{3d-5/2}$ XPS signal intensity increase with the length of the deposition time for InN on Si(100) (a) and GaAs(110) (b) surfaces at 700 K. On Si(100), $In_{3d-5/2}$ XPS signal quickly reached and remained at a value corresponding to about 1 monolayer TMIn adsorbed on the surface (solid circles). No InN film formed on Si(100) without laser irradiation within 24 h. However, when a 308-nm photon beam was used, InN film built up on the surface after an induction time of about 9 h as indicated by the increase of the $In_{3d-5/2}$ signal. It then reached a saturation value because of the XPS detecting limit rather than a termination of the film growth [10]. On the other hand, InN film could be formed on GaAs(110) surface with a shorter induction time and without laser assistance.

Figure 3 details the $Ga_{2p-3/2}$ (a), $As_{2p-3/2}$ (b), $In_{3d-5/2}$ (c) and N_{1S} (d) XP spectra by scanning over smaller energy ranges after InN deposition of 0, 1.5, 6 and 18 h. For the clean surface, $Ga_{2p-3/2}$ and $As_{2p-3/2}$ XPS showed peaks at 1116.6 and 1322.0 eV, respectively. These peaks could be fitted well with a single mixed Gaussian-Lorentz distribution. After deposition for 1.5 h, these peak intensities attenuated by ~60% due to the suppressing effect of the InN overlayers. In addition, a new peak at 1324.3 eV appeared in the $As_{2p-3/2}$ XP spectrum. This broad peak can be further deconvoluted into two components at 1323.8 and 1324.6 eV attributable to AsN and AsN_2, respectively [13].

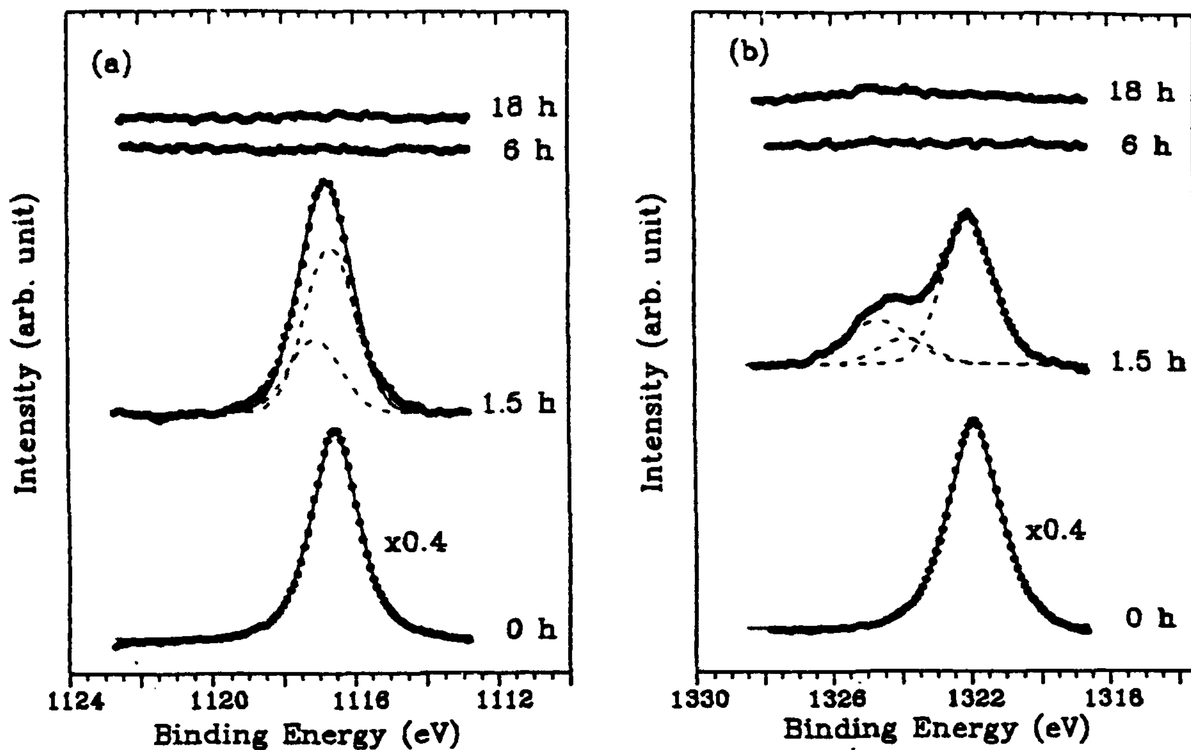

Fig. 3 (a) $Ga_{2p\ 3\ 2}$ and (b) $As_{2p\ 3\ 2}$ XP spectra taken from InN on GaAs at the indicated deposition times with Mg and Al X-ray sources, respectively.

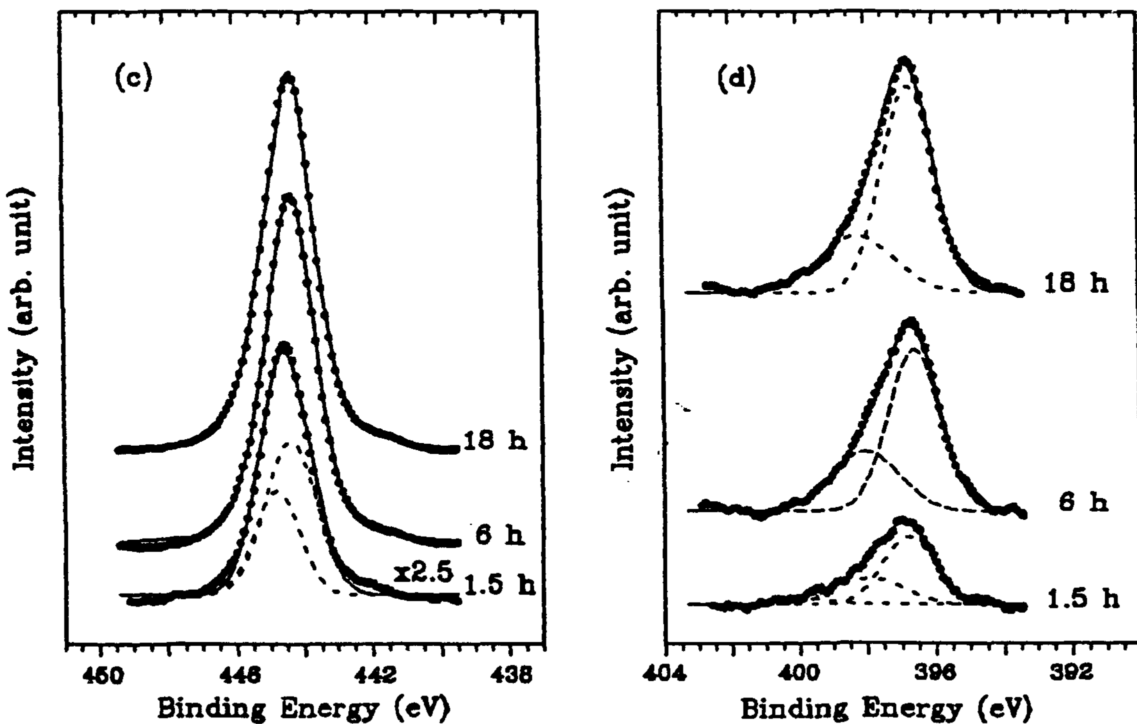

Fig. 3 (c) $In_{3d\ 5\ 2}$ and (d) N_{1s} XP spectra taken from InN on GaAs at the indicated deposition times using Mg X-ray source.

The $Ga_{2p-3/2}$, XPS peak became broader, shifted to 1116.9 and could be deconvoluted into two components at 1116.6 and 1117.1 eV due to substrate and nitride Ga atoms, respectively [13,14]. Meanwhile, the $In_{3d-5/2}$, and N_{1s} photoelectrons presented peaks at 444.6 and 399.9 eV, respectively. The $In_{3d-5/2}$ peak could be deconvoluted into two peaks at 444.4 and 444.7, which are attributable to InN and InN with N atom bonded to the surface atoms, respectively [8, 10]. The N_{1s} XP spectrum could also be fitted with two Gaussian distributions peaking at 396.8 and 398.1 eV. The former peak should have contributions from N atoms bonded to Ga (396.6) and In (396.6) or the combination of them. The 398.1 eV peak is due to the N atoms bonding to As and NH species likely in the form of Ga-NH-As. Both N_{1s} and $In_{3d-5/2}$ peak intensities increased with increasing of the InN deposition time. At 6 h, the 444.4 eV peak dominated $In_{3d-5/2}$ XP spectrum because of the further formation of InN on the surface. The accompanying N_{1s}, XP spectrum also showed a major peak at 396.6 eV due to the InN species, while the 398.1 eV component shifted to 398.2 eV. The latter peak could be attributed to the NH species on InN surface, since the substrate XP signals vanished already under the same experimental conditions (see Figs. 1, 3a and 3b). Further deposition caused no obvious XP spectra changes due to the XPS detecting limit.

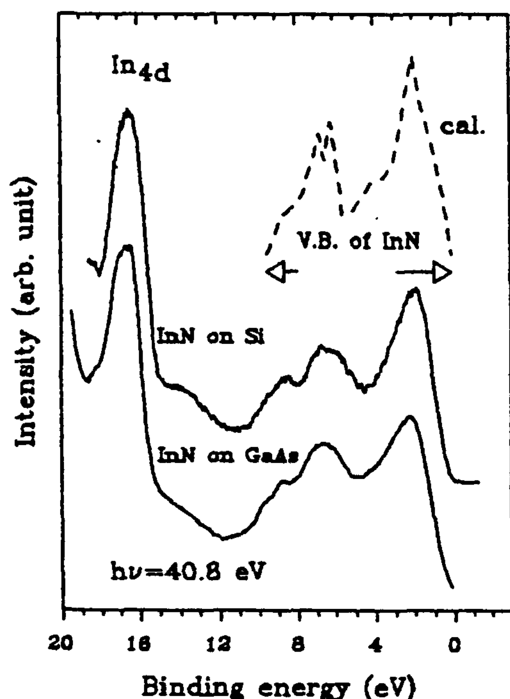

Fig. 4 He(II) UP spectra of InN on GaAs and Si (dashed line is a pseudo-potential calculation)

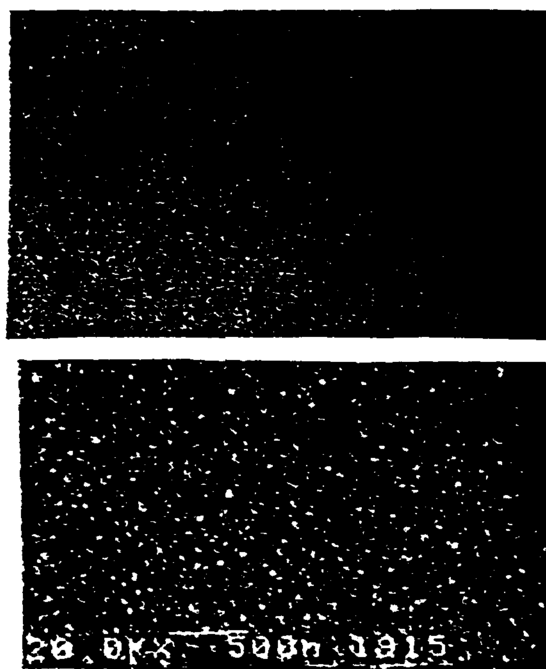

Fig. 5 SEM of InN on GaAs(top). and Si(bottom) substrates.

Figure 4 shows He(II) UP spectra for InN film on GaAs(110) after 18 h of deposition and on Si(100) after 24 h deposition with 308-nm laser irradiation. For comparison, a pseudo-potential calculation for InN valence band by Foley and Tansley is also plotted in the figure as the dashed line. The 16.6 eV peak due to In_{4d} photoelectrons was not given in the calculated curve.

Figure 5 compares SEM pictures taken from InN films on GaAs (a) and Si (b). The samples used here are the same as those for Fig. 4. In contrast to the case of InN on Si(100), where islands of about 100 nm in diameter were observed, InN film on GaAs(110) showed a much smoother surface with no grains being observed at a magnification of 100,000. The particle in the picture, likely a speck of dust, was chosen for the sake of focus.

DISCUSSION

XPS

The growth of InN on GaAs(110) at 700 K bas been monitored using XPS technique and the formation of surface nitrides at the initial deposition process was clearly indicated in the XP spectra as shown in Fig. 3. After a deposition time of 1.5 h, $Ga_{2p-3/2}$ XPS intensity decreased by ~60% and the peak could be deconvoluted into two components at 1116.6 and 1117.1 eV due to Ga atoms in substrate and those bonded to N atoms, respectively. The 1117.1 eV peak is about 0.7 eV lower than the value of 1117.8 observed for GaN [13,14], likely because of the fact that the N atom is bonded to an In atom simultaneously. Similar changes were noted in the $As_{2p-3/2}$ XP spectrum. In addition to the substrate As peak at 1322.0 eV, two peaks at 1323.8 and 1324.6 eV appeared in the spectrum. These peaks have also slightly lower binding energies than those of 1324.0 and 1325.4 eV observed for As nitrides without In atoms [13]; this is consistent with the argument that the N atom is bonded to an In atom as well. Further supporting evidence is that the $In_{3d-5/2}$ peak could be deconvoluted into two components at 444.4 and 444.7 eV. The former peak is due to In in InN, while the latter is due to the InN in which the N atom is back-bonded to surface As and/or Ga atoms. The corresponding N_{1S} XPX result is less conclusive, because the binding energies for GaN, InN and AsN are too close to be separated in the present study. Nevertheless, the peak at 396.8 eV, which is higher than the value of 396.6 for In and Ga nitrides, could be partially attributed to the N atoms bonded to In atoms also.

Further deposition of InN caused the increase of InN signals, i.e., the 396.6 and 444.4 eV peaks for N_{1S} and $In_{3d-5/2}$, respectively, and the decrease of all other XPS signals. Meanwhile, the In:N atomic ratio also increased because of the reduced contribution from other nitrides (GaN and AsN for example) to the N_{1S} XP spectrum. After about 6 h of deposition, the XPS signals from the substrate disappeared and N_{1S} as well as $In_{3d-5/2}$ signals reached their saturating values due to the limited electron escaping length for these photoelectrons (~20 Å). In addition, the In:N atomic ratio is now about 0.9, if the photo-emission cross-section for N_{1S} and $In_{3d-5/2}$ is taken into account [15]. This value becomes 1.1, if we exclude the 398.2 eV component for the NH species, which was also observed in the deposition process of InN on Si(100), according to the N_{1S} XP spectrum. The In:N atomic ratio of our deposited film therefore averaged to be 1.0±0.1, indicating a stoichiometric or nearly stoichiometric growth of InN film under the indicated experimental conditions. Further growth of InN cannot be characterized by the XPS method.

Another interesting and important observation is the absence of an obvious C XPS signal, which suggests that C contamination is not as serious as that implied by the thermal decomposition study of TMIn on Si substrates. We found that partial CH_x species remained on the surface at temperatures higher than the In atom desorption temperature [12]. Similar observations were reported for TMAl and TMGa on Si substrates [16,17]. Clearly, the reaction mechanisms are different in the thermal decomposition of TMIn on Si from that in the InN film deposition process. In the latter case, the formation of the InN bond may facilitate the release of CH_3 radicals.

UPS

The InN films were also characterized with the UPS technique. Representative spectra for InN on both GaAs(110) and Si(100) are shown in Fig. 4. The two spectra are nearly identical, indicating that the substrate contribution to the spectra is negligible. This observation is consistent with those observed from XPS measurements, where no substrate signals could be detected either. The He(II) UP spectra also compare favorably with the result of a pseudo-potential calculation for InN valence band [18] (dashed line in Fig. 4). A peak at ~2.1 eV appeared in all spectra, however, the doublet at 6.5 and 7.1 eV was not resolved in our UP spectra. Instead, a single broad peak centered at ~6.6 eV was observed and the shoulder at ~8.5 eV was more pronounced. Accordingly, the overall valence band widths of our UP spectra are greater than that gleaned from the calculation. The most intense peak at ~16.6 eV is originated from In_{4d} electrons, which was not presented in the theoretical calculation but was observed in the UP spectrum for TMIn adsorbed on Si substrates [12].

CONCLUSION

The deposition of InN thin films on GaAs(110) using HN_3 and TMIn has been studied with XPS, UPS and SEM. In contrast to InN on Si(100), InN films could be formed on GaAs(110) at 700 K without 308-nm laser irradiation, which is necessary for the growth of InN film on Si(100). Under the present experimental conditions, $In_{3d_{5/2}}$ XPS signal reached a saturation value after ~6 h of deposition due to the XPS detecting limit rather than the termination of film growth. Meanwhile, the In:N atomic ratio increased to 1.0±0.1 and remained unchanged with further film deposition, indicating a stoichiometric or nearly stoichiometric growth of InN on GaAs(110). Similar results were found for the deposition of InN on Si(100) with 308-nm laser assistance. The He(II) UP spectra taken from InN films on GaAs(110) and Si(100) are nearly identical and agree reasonably well with a pseudo-potential calculation for the InN valence band. The corresponding SEM analyses showed smooth InN films on GaAs(110), however, grains with diameter of ~100 nm were observed for InN on Si(100) at a magnification of ≥20,000 X.

The fact that InN film can be deposited on GaAs(110) using TMIn and HN_3 beams, but not on Si(100) without laser irradiation may be due to the following factors which inhibit the growth of InN on Si(100): 1. NH species was found to be stable up to 800 K on Si substrate; 2. The different chemical properties of Si and InN; and 3. The lattice mismatching for Si(100)-2x1 and InN as listed below:

Si(100)-2x1	a_1=2.3, a_2=5.4	GaAs(110)	a=3.997	InN	a=3.548
	b=3.8		b=5.66		c=5.76
Si(100)	a=b=3.8				

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