$Si_{1-x-y}Ge_xC_y$ Layers: Growth and Characterization

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We report on the structural and optical properties of silicon-based heterostructures containing ternary $Si_{1-x-y}Ge_xC_y$ alloys. Both single and multiple quantum wells were grown by molecular beam epitaxy and their quality was assessed by x-ray rocking analyses and by photoluminescence (PL) measurements. Optimum growth temperatures with respect to carbon incorporation and layer quality were found to be at around 500°C. We observed well behaved PL signals from $Si_{1-y}C_y$ single layers and Si/ $Si_{1-y}C_y$ multiple quantum wells as well as from $Si/Si_{1-y}C_y/Si_{1-x}Ge_x$ superlattices with carbon concentrations up to 1.7%. For an investigation of the thermal stability of these intrinsically metastable layers, ex-situ annealing experiments were conducted in the temperature range between 500°C and 900°C. Up to about 725°C an improvement of the PL signals both with respect to intensity and linewidth is observed, whereas the amount of substitutional carbon remained unaffected. After annealing at 725°C we observed the narrowest linewidth in a $Si_{1-y}C_y$ single layer reported so far in the literature. At higher annealing temperatures the PL signal decreases, but it takes more than 850°C to observe a decrease of the substitutional carbon concentration in x-ray measurements. The results indicate that carbon containing epi-layers of high crystal quality can be grown by MBE, and that thermal stability is good enough to make the material interesting for device applications.

1. Introduction

It is the outstanding property of Si-based heterostructures to provide the application relevant combination of bandstructure engineering and silicon very-large-scale-integration (VLSI) compatibility. In the past few years most of the basic properties regarding the lattice mismatched $Si/Si_{1-x}Ge_x$ material combination, and especially the effects of strain on the band offsets and bandgaps, have been investigated [1]. It has been found that the band offset at the interface between a pseudomorphic $Si_{1-x}Ge_x$ layer and a Si substrate occurs almost exclusively in the valence bands, whereas a tensilely strained Si layer is required for the implementation of useful conduction band offsets. By employing proper combinations of pseudomorphic and strain-relaxed epi-layers, both tensile and compressive strains can be custom designed, without sacrificing the important advantages of a Si substrate and the basic compatibility with Si technologies.

By exploiting *strain-engineering* as an additional degree of freedom, a wide variety of devices structures have been implemented in the $Si/Si_{1-x}Ge_x$ material system, reaching from heterobipolar transistors (HBT) [2] over p- and n-type modulation-doped field effect transistors (MODFET) [3] to optical detectors in the near infrared, and even light emitters [4]. Nevertheless, so far only the pseudomorphic Si/SiGe HBT has reached production status, whereas other devices with demonstrated superior properties, such as the n-type MODFET, are still restricted to test devices on a laboratory level. The main reason for the much slower development of the MODFET lies in the necessity for strain

relaxed $Si_{1-x}Ge_x$ buffer layers. These have successfully been implemented by several research groups [5] – [7], but defect and morphology control still require further refinement to make them suited for a production environment.

Ternary $Si_{1-x-y}Ge_xC_y$ alloys offer an alternative route to strain-engineering in silicon-based heterostructures, which finally may overcome the problems imposed by relaxed buffer layers: Due to the covalent radii of C and Ge, which are smaller, and larger than that of Si, respectively, both compressively and tensilely strained, pseudomorphic layers can be implemented by proper adjustment of x and y in the active layers of a heterostructure [8]. However, in contrast to the binary $Si_{1-x}Ge_x$ alloys, which are thermodynamically stable for all compositions x, carbon has almost negligible solid solubility in both Si and Ge, but, on the other hand, tends to the formation of stoichiometric SiC. Since strain engineering requires C concentrations of a few percent to provide useful modifications of the band structure [9], non-equilibrium growth conditions at sufficiently low temperatures have to be established. This requires an optimization of the growth parameters to allow sufficiently high C incorporation without excessive degradation of the crystal quality through the undesirable generation of point defects. Also, the surface morphology has to be controlled in order to suppress strain-induced three-dimensional growth.

In the following we report on the progress that has been made in Linz regarding the growth of heterostructures containing ternary $Si_{1-x-y}Ge_xC_y$ alloys. The main emphasis in 1996 has been put on the structural and optical qualities of these layer sequences, which are an essential prerequisite for any further assessment of the future role $Si_{1-x-y}Ge_xC_y$ alloys can play in the field of application-driven band structure engineering.

2. Sample Preparation and Characterization

The ternary $Si_{1-x-y}Ge_xC_y$ alloys were grown in a newly commissioned RIBER SIVA 45 MBE machine equipped with electron beam evaporators for Si, Ge, and C, and dopant effusion cells for Sb (n-type) and B (p-type). High-purity, single crystalline ingots are used for the Si and Ge sources, whereas pyrolytic graphite is used in the carbon evaporator. The fluxes of all three matrix materials are monitored, and feedback-controlled, by a quadrupole mass spectrometer with a cross-beam ion source and PID controllers. The mass spectrometer signals are calibrated by epitaxial growth of $Si_{1-x}Ge_x$ and $Si_{1-y}C_y$ reference layers, the compositions and layer thicknesses of which are determined by x-ray rocking analyses in combination with dynamic simulations. The flux stability, especially of the C source, which is the most critical one because of the small fluxes required, is occasionally checked by quantitative SIMS analysis.

High-resistivity (FZ, $\rho > 1000\ \Omega$cm) Si substrates of 100 mm diameter are chemically precleaned either by oxide removal in 5% HF or by a standard RCA cleaning procedure. Immediately after precleaning the wafers are mounted in 125 mm diameter, all-silicon adapters, a total of six of which can be introduced into the magazine of the load-lock chamber. After pump-down of the load-lock chamber into the 10^{-9} mbar range, the wafers are transferred into the growth chamber, where they are suspended by Mo-clamps underneath a radiative substrate heater made of pyrolytic graphite (PG). Prior to growth, which always commences with a Si buffer layer of 100 to 200 nm thickness, a thermal cleaning step is performed at 900 °C for typically 5 min to remove SiO_2 and possible organic contaminations from the surface. This step can be controlled by in-situ reflec-

tion high energy electron diffraction (RHEED), which reveals a (2x1) reconstruction of the bare Si surface as soon as the amorphous oxide has been flashed off.

The heterostructures are routinely characterized by x-ray diffraction, which yields, as mentioned, in the case of single layers composition and layer thickness. In the case of multiple quantum wells, and superlattices the period length is the primary information derived from rocking measurements. The compositions and the thicknesses of the individual layers can also be extracted by fitting of dynamic simulation curves, however, a certain degree of ambiguity remains. For that reason additional information is useful, such as the composition determined by SIMS analysis, or Rutherford backscattering (RBS). The latter technique is not directly applicable to C, because of the minor backscattering yield from the light elements. Therefore, we are presently trying in collaboration with the University of Padua to exploit a nuclear resonance with broad enough scattering cross section to enhance the back scattering yield to an extent that allows for an absolute, depth resolved evaluation of the carbon content.

For an investigation of the thermal stability of the strained $Si_{1-y}C_y$ layers annealing at temperatures between 500 °C and 900 °C was performed under vacuum either in a furnace or directly in the MBE growth chamber.

Photoluminescence (PL) spectroscopy is a versatile technique, which not only provides information on the band gaps and the band offsets, but is also a sensitive indicator of the overall crystal quality of the layers. This is of special interest for an optimization of the low temperature growth conditions required for the metastable incorporation of carbon, because the PL signal is strongly suppressed, once the density of growth-induced non-radiative recombination centers becomes too high. For our investigations, PL was excited by the 488 nm line of an Ar^+ laser, analyzed in a 0.32 m grating spectrometer and detected by a North Coast Ge detector in a standard lock-in technique. A temperature-variable He cryostat allowed for temperature dependent measurements in the range between 1.6 and 300 K.

3. Experimental Results

Three types of samples were grown for these studies, namely $Si_{1-y}C_y$ single layers, $Si/Si_{1-y}C_y$ multiple quantum wells, and strain compensated $Si/Si_{1-y}C_y/Si_{1-x}Ge_x$ superlattices. In the first two types of samples the band offset is almost exclusively restricted to the conduction band, which is energetically lower in the tensilely strained $Si_{1-y}C_y$ layers due to a strain splitting of the six-fold degenerate, Si-like conduction band. The situation is analogous to strained Si grown on a relaxed $Si_{1-x}Ge_x$ buffer layer and is therefore of special interest for the implementation of n-type MODFETs. Band alignment in the $Si/Si_{1-y}C_y/Si_{1-x}Ge_x$ superlattices, which are interesting for infrared detector applications because of the inherent strain compensation, is more complex: Since the $Si_{1-x}Ge_x$ layers introduce an additional valence band offset, carrier confinement is indirect both in k-space and in real space, with electrons being located in the $Si_{1-y}C_y$ layers and holes in the $Si_{1-x}Ge_x$ layers.

At growth temperatures of around 500 °C the as-grown samples of all three types showed well behaved PL signals. There is presently only one other group worldwide that has published comparable PL spectra from MBE-grown layers [10]. As an example, Fig. 1 shows the spectrum of a ten-period $Si/Si_{0.989}C_{0.011}/Si_{0.9}Ge_{0.1}$ superlattice together with a schematic view of the strain-induced band alignment. Two distinct peaks are observed, which originate from band edge recombination in the vicinity of the $Si_{1-y}C_y$/

$Si_{1-x}Ge_x$ interface, where the wave functions of electrons and holes have finite overlap. The peak at higher energies, labeled SiC-NP, results from the no-phonon transition, whereas the other peak is its TO phonon replica. A NP transition in an indirect gap material is only possible if symmetry breaking mechanisms are present, such as the presence of a heterointerfaces and/or the statistical fluctuations in a random alloy, which is both the case in our layers. The relative strength of the superlattice related peaks can be judged by comparison with the TO replicas originating from the Si layers and from the substrate. Obviously, the quantum wells very efficiently collect electron-hole pairs from the several µm deep excitation volume, and also maintain long enough lifetimes to allow the observation of radiative recombination. The strength of the bandgap PL signal is therefore an important indicator of the crystal quality, since an excessive amount of defects in the layers and at the heterointerfaces associated with non-radiative recombination would quench the PL signal altogether. This is indeed the case, when growth temperatures below 450°C are employed.

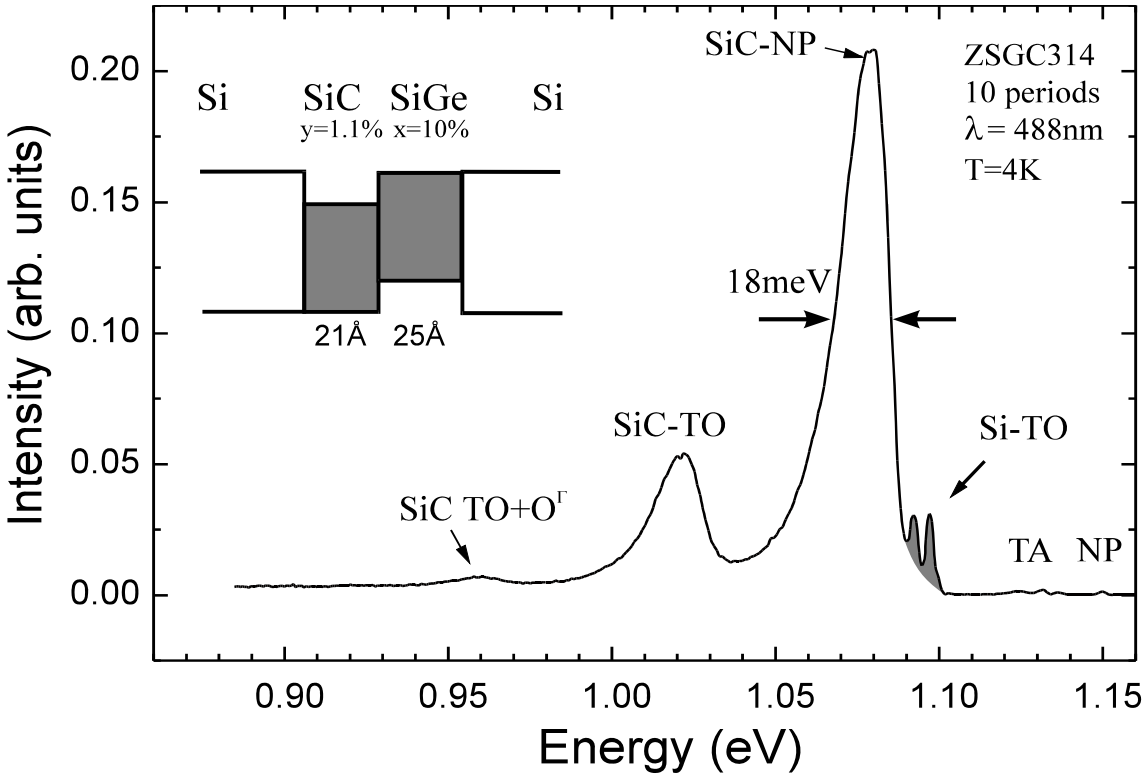

Fig. 1: PL spectrum of a ten-period $Si/Si_{0.989}C_{0.011}/Si_{0.9}Ge_{0.1}$ superlattice. The dominating signals are the no-phonon (NP) band edge recombination from the quantum well section and its TO-phonon replica. The shaded part of the spectrum results from the Si layers and the Si substrate.

Compared to the well established quantum well luminescence from single $Si_{1-x}Ge_x$ layers [11], the PL signal in Fig. 1 is almost a factor of six broader. Since close to a factor of ten higher Ge concentrations are required to induce the same amount of strain that is provided by a given carbon concentration, the statistical fluctuations of both the well width and the well depth are much more pronounced in the case of a $Si_{1-y}C_y$ layer of comparable average strain. In addition possible composition fluctuations from layer to layer may contribute to the line width from a superlattice. For the investigation of

annealing effects we therefore mainly concentrated on single $Si_{1-y}C_y$ layers, which were grown thin enough to remain with the critical thickness limitations, but thick enough to suppress quantum confinement effects. Save for the exciton binding energy, this way the true band gap recombination is measured without any necessity for the correction of confinement energies. In addition, cross checks with the multiple quantum well samples confirmed that the annealing behavior is qualitatively the same.

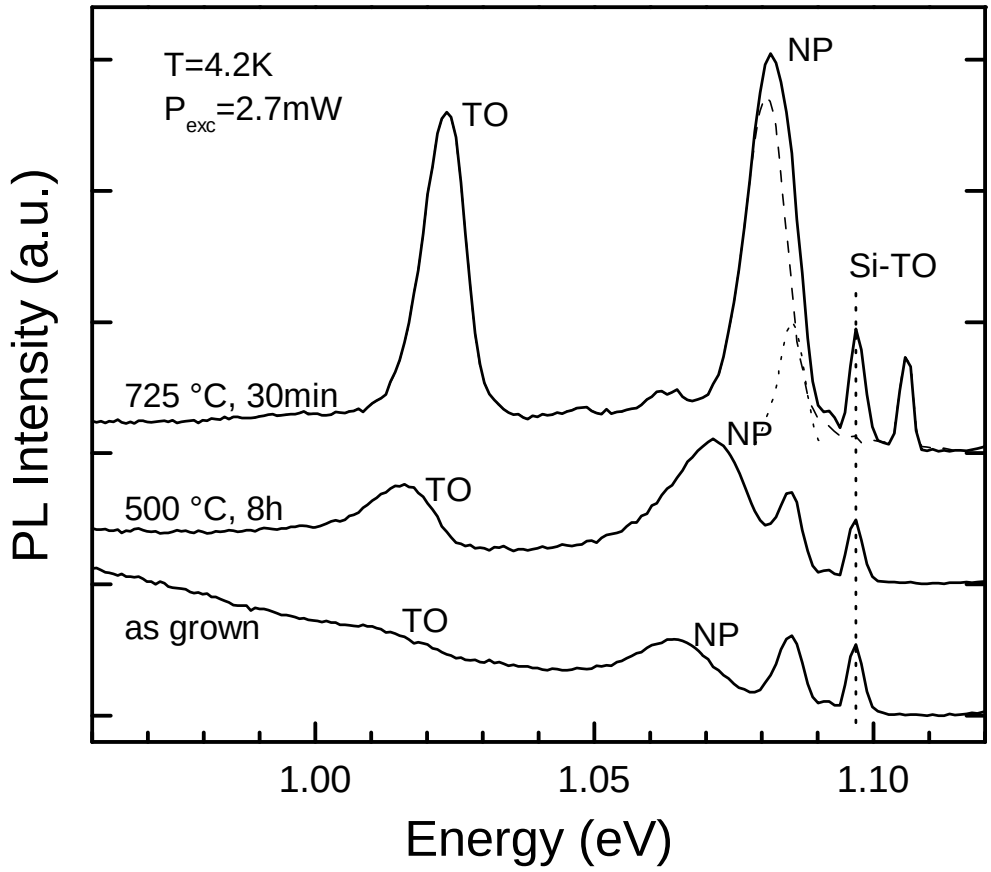

Fig. 2: Evolution of the PL signal of a single $Si_{1-y}C_y$ layer for increasing annealing temperatures. Note the blue shift and the line narrowing.

Figure 2 shows a series of PL measurements from a 100 nm thick $Si_{0.989}C_{0.011}$ layer, which underwent annealing at successively higher temperatures in the range between 500 and 725 °C. There are three main effects associated with annealing: (i) The intensity of the band gap PL signal increases significantly within the range of annealing temperatures shown here. (ii) There is a noticeable *blue shift* of the PL lines amounting to about 15 meV. (iii) The line width after background subtraction becomes much narrower as the annealing temperature is increased. In fact, the linewidth of 8.4 meV in the topmost curve of Fig. 2 is the narrowest observed to date in a $Si_{1-y}C_y$ layer.

Most interesting, the pronounced changes of the PL signal are not associated with a change of the substitutional carbon concentration, as has been checked by x-ray rocking analyses. Only at higher annealing temperatures of >850 °C a loss of substitutional carbon is observed, whereas the PL intensity starts decaying already at about 750 °C.

Since changes of the *average* C concentration can be ruled out, and quantum confinement effects through possible short range diffusion of substitutional carbon can be neglected in the thick layers used here, the development of the PL signal has to have other reasons. To further elucidate these mechanisms, PL measurements of the samples with the highest PL intensity were recorded as a function of the measurement temperature. This is shown in Fig. 3, where the TO-replica of the band gap recombination, which is not affected by spurious signals from the Si substrate, is plotted for measurement temperatures in the range between 4.2 and 20K. The most striking feature of these measurements, which was confirmed by experiments on the quantum well samples, is a *red shift* concomitant with a decay of the intensity as the temperature is increased.

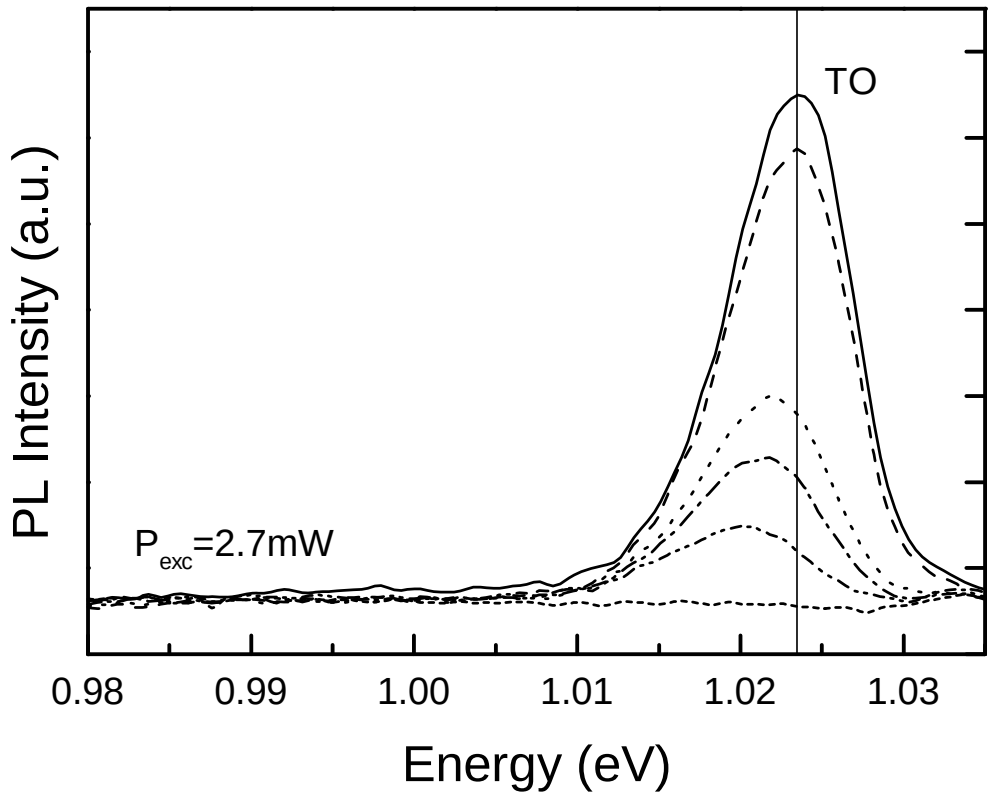

Fig. 3: Red shift of the PL signal with increasing measurement temperature. The TO-phonon replica is plotted here, because it is free of substrate-related signals.

4. Discussion

A consistent interpretation of the annealing effects and of the red shift with higher measurement temperature can be derived, when assuming that the as-grown samples contain non-radiative recombination centers as well as non-statistical fluctuations of the local, substitutional carbon concentration. The latter may be associated with C_2 and C_3 molecules, which are observed in the mass spectrum of the carbon molecular beam, and which are tentatively not completely dissociated at the low growth temperatures employed. Based on these assumptions the following effects will occur during annealing:

(i) At low annealing temperatures (middle curve in Fig. 2, 500 °C for 8 h), non-radiative recombination centers associated with growth defects begin to disappear. This leads to an increase of the PL intensity, but only to a minor decrease of the line width.

(ii) At higher annealing temperatures (upper curve in Fig. 2, 725 °C 30 min) a redistribution of carbon on a local scale occurs, which leads to the dissolution of local carbon accumulations, introduced e.g. by molecular forms of evaporated C. The overall effect is a more homogeneous, statistical distribution of carbon, which causes two effects: First, the PL signal experiences a blue shift, because homogenization of the carbon concentration smears out the local band gap minima in regions of originally enhanced concentration. Second, the line width becomes narrower as the statistical fluctuations become smaller. This interpretation is corroborated by the fact that the ratio between NP signal and TO-replica decreases, which means a reduction of the symmetry-braking alloy fluctuations.

(iii) Although the fluctuations of the carbon concentration become more homogeneous upon annealing, the remaining alloy is still random. This explains the red shift with increasing measurement temperature, which results from carriers bound to alloy fluctuations, as has been observed in $Si_{1.x}Ge_x$, too [12]. With increasing temperature the electrons become mobile and establish an equilibrium distribution that preferentially fills the regions with the smallest band gaps.

(iv) The layers are thermally stable to beyond 850 °C, with no indications for a change of the average concentration of substitutional carbon. Thus noticeable diffusion of carbon or SiC precipitation requires higher temperatures and should not be a severe limitation for device processing.

5. Conclusions and Outlook

We have established MBE growth conditions for high-quality $Si/Si_{1-y}C_y$ and $Si/Si_{1-y}C_y/Si_{1-x}Ge_x$ samples with substitutional carbon concentrations of up to 1.7 %. Well-behaved PL signals from band edge recombination in the $Si_{1-y}C_y$ layers, and at the $Si_{1-y}C_y/Si_{1-x}Ge_x$ interface, respectively, have been observed. The quality of the layers improves significantly upon annealing at moderate temperatures of about 725 °C, without affecting the substitutional carbon concentration. At these temperatures annealing mainly reduces the defect density in the layers and leads to a more homogeneous distribution of substitutional carbon. The layers are thermally stable to beyond 850 °C, where we observe first indications for a reduction of the substitutional carbon content.

Successful growth of carbon-containing, Si-based heterostructures is an important prerequisite for a future implementation of n-type MODFETs with tensilely strained $Si_{1-y}C_y$ quantum wells. In a next step growth conditions have to be adjusted to allow somewhat higher carbon concentrations of about 2 – 2.5 %, which are necessary for the required conduction band offset of 130 to 160 meV. Such layers will allow the fabrication of MODFETs for an assessment of the electronic properties.

Acknowledgments

Discussions with J. Stangl and G. Bauer, and financial support by the Fonds zur Förderung der wissenschaftlichen Forschung (FWF) are gratefully acknowledged. C.P. is supported by a scholarship from the Österreichische Akademie der Wissenschaften.

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