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# The Control of Stoichiometry in Epitaxial Semiconductor Structures: Interfacial Chemistry - Property Relations

A Workshop Review

by

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## 1. Introduction

A workshop on the control of stoichiometry in epitaxial semiconductor structures was held on August 21-26, 1995 in the hotel Stutenhaus at Vesser in Germany<sup>1</sup>. The secluded location of the workshop in the forest of Thuringia and its informal style stimulated extensive private discussions among the participants and promoted new contacts between young scientists from Eastern and Western Europe and the USA. Topics addressed by the presentations were interactions of precursors to heteroepitaxy and doping with the substrate surface, the control of interfacial properties under the conditions of heteroepitaxy for selected materials systems, methods of characterization of interfaces and native point defects in semiconductor heterostructures and an in-depth evaluation of the present status of the control and characterization of the point defect chemistry for one specific semiconductor ( $\text{ZnGeP}_2$ ), including studies of both heterostructures and bulk single crystals. The selected examples of presentations and comments given here represent individual choices - made by the author to highlight major points of the discussions.

## 2. Precursor-Surface Interactions and Control of Heteroepitaxial Processes

The workshop kick-off was provided by Prof. R. Hamers of the University of Wisconsin at Madison, USA, who considered the close link between surface composition, structure and reactivity for the examples of phosphine and diborane interactions with the  $\text{Si}(001) 2 \times 1$  surface at elevated temperature. While at moderate coverage dispersed Si-P heterodimers are formed upon phosphine dosing, the boron atoms on the  $\text{Si}(001)$  - formed upon dosing with diborane - tend to cluster. On the  $\text{PH}_3$ -dosed  $\text{Si}(001)$  surface inhibition of both  $\text{PH}_3$  adsorption and decomposition is observed. On the phase separated diborane-doped  $\text{Si}(001)$  surface the concomitant spatial variations in the reactivity result in roughening upon Si overgrowth by silane decomposition.

Thus early surface interactions of impurities affect in a significant way subsequent stages of epitaxial growth. Prof. M. Greenief of the University of Missouri-Columbia, USA, investigated the precursor-mediated adsorption of  $\text{GeH}_{3-x}\text{Et}_{1+x}$  ( $x = 0, 1$ ) on the  $\text{Si}(001)$   $2 \times 1$  surface in the context of the possible utility of substituted germane for atomic layer epitaxy (ALE) of  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}$  heterostructures. Dr. U. Rossow of North Carolina State University, USA, presented results of optical real-time process monitoring for the example of  $\text{Ga}_x\text{In}_{1-x}\text{P}$  heteroepitaxy on  $\text{Si}(001)$  ( $2 \times 1$ ) by pulsed chemical beam epitaxy (CBE). Combination of several complimenting methods (p-polarized reflectance spectroscopy, reflectance difference spectroscopy, laser light scattering) is essential for unraveling the complex surface kinetics that is encountered under actual growth conditions. Simultaneous changes in surface composition, reconstruction and roughness must be considered that depend on the history of initial surface conditioning, nucleation and overgrowth of the substrate surface and the evolution of the subsequent steady state growth. Thus there exist principal differences that are difficult to bridge between dosing experiments of clean surfaces and non-intrusive real-time process monitoring of dynamic growth processes.

Further details of  $\text{Si}_x\text{Ge}_{1-x}$  growth on Si were added for a variety of methods of heteroepitaxy. Dr. Grutzmacher of the Paul Scherrer Institute at Villingen, Switzerland, presented results - obtained by X-ray reflectivity and photoluminescence studies for  $\text{Si}_x\text{Ge}_{1-x}/\text{Si}$  heterostructures that were grown by molecular beam epitaxy (MBE) and chemical vapor deposition (CVD). The roughness of the  $\text{Si}/\text{Si}_x\text{Ge}_{1-x}$  interface is determined by Ge segregation and islanding. Under the conditions of atmospheric pressure CVD, Ge segregation is suppressed by hydrogen passivation of the silicon surface, and the interfacial roughness is less than 2 monolayers at growth temperatures  $500^\circ\text{C} \leq T \leq 750^\circ\text{C}$ . Under the conditions of ultra-high vacuum CVD and MBE, temperatures  $\leq 500^\circ\text{C}$  and  $400^\circ\text{C}$ , respectively, are required to achieve comparable interface abruptness. Since the energy eigenvalues associated with quantum well states are broadened by interface roughness into sub-bands, the above results are important for the properties of confined heterostructure devices. For example, the peak-to-valley ratio in the current-voltage characteristics of double-barrier resonant tunneling diodes (RTDs) is severely curtailed by interface roughness.  $\text{Si}/\text{Si}_x\text{Ge}_{1-x}$  RTDs - made in Dr. Grutzmacher's laboratory by atmospheric pressure CVD - exhibit peak-to valley ratios of 4.2:1 and 1.5:1 for the light and heavy hole subband energy level related features in the current-voltage characteristics, respectively. Prof. Sturm of Princeton University, USA, reported on  $\text{Si}_x\text{Ge}_{1-x}/\text{Si}$  and  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y/\text{Si}$  heteroepitaxy by rapid thermal CVD under ultra-clean conditions, that is, partial pressures of oxygen and water vapor  $\ll 100\text{ppb}$ . Photoluminescence studies reveal that the bandgap increase expected for pseudomorphic growth is overcompensated by the reduction in the bandgap due to the reduction of strain upon carbon incorporation into the  $\text{Si}_x\text{Ge}_{1-x}$  film. In addition to strain relaxation by size compensating C-doping, strain relaxation for  $\text{Si}_x\text{Ge}_{1-x}$  alloys by native point

defects that segregate to the  $\text{Si}_x\text{Ge}_{1-x}$  film was investigated on the basis of  $\text{Si}^+$  ion implantation experiments. The topic of ion beam processing was further developed by the presentations of Prof. Grob of the CNRS at Strasbourg, France, and Prof. Romanyuk of the Institute of Semiconductor Physics at Kiev, Ukraine, focusing onto the growth of  $\text{Si}_x\text{Ge}_{1-x}$  and SiC, respectively, in Ge and C-implanted Si upon annealing. The sputtering limits to high dose implantation, the use of multiple implants of carbon and oxygen, the gettering oxygen into the C-implanted region, and the dissolution of precipitates due to Ostwald ripening are important aspects of attaining subcutaneous compound films with sharp interfaces. In view of the interest in the heteroepitaxy of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  that lattice matches SiC and the lack of affordable SiC substrates, in the opinion of the author, research on SiC-on-Si heterostructures is bound to receive renewed attention, but represents a considerable challenge. Prof. Scholz of the Max-Planck Institute für Mikrostrukturtechnik at Halle, Germany, presented the results of transmission electron microscopy investigations of defects in SiC-on-Si heterostructures grown by carbonization of the Si surface followed by SiC epitaxy using  $\text{SiH}_4$  and various choices of carbon source gases. Planar defects, that is, twins, stacking faults and inversion domain boundaries on singular Si surfaces, misfit dislocations, pyramidal voids formed due to outdiffusion of silicon in the initial stage of surface carbonization and pits/hillocks on the surface of thicker SiC epilayers are observed and present impediments to the successful use of SiC-on-Si as substrates for subsequent group III nitride growth. The causes for the formation of these defects are not completely understood at present and warrant further investigation.

Dr. Hong of AT&T Bell Laboratories provided a comprehensive review of molecular beam epitaxy in the context of in-situ processing that, for example, allows surface cleaning by ECR  $\text{H}_2$  plasma etching/ $\text{Cl}_2$  chemical etching, the anisotropic deep etching of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  using  $\text{SiCl}_4$  ECR plasma etching, in-situ deposition of high quality Schottky contacts and non-alloyed ohmic metal contacts on GaAs, and the fabrication of in-situ deposited oxide/GaAs structures with low interface state density. Several examples of applications of integrated processing (e.g., advanced laser structures for optical communications and compound semiconductor IGFETs) were discussed. The key message of Dr. Hong's review was that maintaining tight control over the composition and structure of interfaces and free surfaces in all steps of a complex processing sequence permits the realization of device structures that are unattainable otherwise and is essential for assuring high performance and reliability. Prof. Kolodziejwski of the Massachusetts Institute of Technology, USA, extended the discussion of compound heterostructures to heterovalent interfaces composed of II-VI and III-V compounds. Motivated by the present interest in blue light emitting diodes and heterostructure lasers employing  $\text{Mg}_x\text{Zn}_{1-x}\text{S}_y\text{Se}_{1-y}$  alloy compositions that are nearly lattice-matched to GaAs the presentation focused onto GaAs/ZnSe heterostructures. Since the band offsets at the heterointerface depend critically on the interface

composition/structure the control of the reconstruction of the GaAs substrate surfaces plays an essential role in the control of the properties of ZnSe/GaAs heterostructures. A comprehensive evaluation of the conditions for the growth of both high quality ZnSe on GaAs and GaAs on ZnSe epilayers was provided that enables the fabrication of high quality ZnSe/GaAs quantum well heterostructures, which are presently being explored with regard to their optical properties.

Additional questions that are left open to be addressed in future are:

- (i) Can the concentration of residual impurities on semiconductor surfaces (e.g.,  $\text{OH}^-$ ,  $\text{F}^-$  on Si) ever be made small enough to have a negligible impact on initial stages of heteroepitaxy? In particular, how effective/reliable is burying the impurities in an initial homoepitaxial step for the substrates and classes of compounds considered here?
- (ii) Do compliant substrates technologies alleviate the need for research on the growth of bulk single crystals with tunable lattice constants?
- (iii) Is optical real-time monitoring sufficient to determine the kinetics of heteroepitaxial overgrowth, and, if not, which other supplementing methods of non-intrusive real-time monitoring can be added?
- (iv) Is engineered atomic layer epitaxy on the basis of real-time process control eliminating the need for self-limiting mechanisms?
- (v) Will GaAs IGFETs made by integrated MBE processing replace other advanced compound semiconductor or group IV transistors in selected applications?

### 3. Characterization of Interfacial Stoichiometry and Point Defects

The session focusing onto the characterization of interfacial stoichiometry and the point defect chemistry of compound semiconductors was started with a presentation of Prof. Vedel of the Ecole Nationale Supérieure de Chimie de Paris, France, who reviewed electrochemical techniques, such as, the potentiometric measurement of the activity of a selected component in a compound or the controlled changes of its stoichiometry by Coulometric titration (e.g., a binary compound  $\text{A}_{1+\delta}\text{B}$  in an electrochemical cell  $\text{A}'|\text{A}|\text{A}^+, \text{X}^-|\text{A}_{1+\delta}\text{B}|\text{A}'$  becoming richer in A upon passing a positive electrical current from the left electrode A' to the right electrode of the same material). Examples considered were the titration of  $\text{FeO}_x$  using a solid  $\text{ZrO}_2 + \text{CaO}$  electrolyte,  $\text{Al}_{1+\delta}\text{Sb}$  in  $\text{CaF}_2$  and  $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$  in  $\text{ZnCl}_2 + \text{NaCl} + \text{KCl}$  molten salt electrolyte. Several additional presentations addressed physical methods for the characterization of point defects in semiconductors. Prof. Wagner of the Fraunhofer-Institut für Angewandte Festkörperphysik at Freiburg, Germany, provided a stimulating review of Raman spectroscopy, which is a powerful method for the characterization of heterointerfaces, particularly for polar semiconductors, such

as, the III-V compounds. Specific points of this presentation were the investigation of local vibrational modes of impurity atoms, including the transition from isolated impurities to the planar vibrational modes of doping sheets, and the exploitation of resonance effects in the Raman scattering cross section for achieving high sensitivity. The use of radioactive nuclei as probe atoms in semiconductors was discussed by Prof. Mahnke of the Hahn-Meitner Institut Berlin, Germany, with special emphasis on II-VI compounds and their I-III-VI<sub>2</sub> isoelectronic analogs. Examples considered were the study of intrinsic defects and donor-acceptor pair formation in CdTe by perturbed angular correlation (PAC) spectroscopy, and the identification of phases in the Cu-In-S system. Also the use of radioactive isotopes of main constituents in transmutation doping of II-VI compounds was reviewed. Prof. Krause-Rehberg of the Martin-Luther Universitat at Halle-Wittenberg, Germany, discussed the use of positron annihilation (PA) spectroscopy at defects for studies of their concentration, spatial distribution, and ionization energy relative to the band edges. Specific examples discussed were positron trapping at dislocations, vacancy defects and vacancy clusters for which the lower sensitivity limits are 10<sup>8</sup> cm<sup>-2</sup>, 10<sup>15</sup> cm<sup>-3</sup>, and 10<sup>14</sup> cm<sup>-3</sup>, respectively. Dr. Gerhardt of the Institut fur Kristallzuchtung, Berlin, Germany, presented results on the optical determination of the Ge-content in bulk Si<sub>x</sub>Ge<sub>1-x</sub> single crystals grown by float-zoning. His presentation showed that through the appropriate choice of the zone composition and growth parameters both segregation effects and constitutional supercooling can be controlled. In the opinion of the author, the expansion of substrate technologies to solid solutions is an important topic of future research. Prof. Koschnick of the University of Paderborn, Germany, provided an overview over the characterization of point defects in III-V compounds by optically detected electron spin resonance (ODESR) and electron-nuclear double resonance (ODENDOR) spectroscopies focusing on the As<sub>Ga</sub>-X<sub>2</sub> defect and substitutional oxygen in GaAs. The ODENDOR shf-interactions provide information on the microscopic structure of defects, and relative defect concentrations can be evaluated from the magnetic circular dichroism of the absorption (MCDA). For example, the ODENDOR-lines observed for the O<sub>As</sub> defect are incompatible with a tetrahedral coordination of the O<sub>As</sub> defect, which is located at an off-center position along (100). Information on the concentrations of the EL2 and O<sub>As</sub> defects in oxygen-doped GaAs can be obtained by studies of MCDA since upon ionization of the EL2 defect according to EL2 → EL<sup>+</sup> + e<sup>-</sup> the electron thus generated is captured by the substitutional oxygen traps. This creates a paramagnetic oxygen state that can be detected in the MCDA. Further examples of the utility of ODESR/ODENDOR in studies of point defects in compound semiconductors were presented by Profs. Giles and Halliburton of the University of West Virginia, USA, in the special section concerning the control of stoichiometry of ZnGeP<sub>2</sub>.

Questions that, in the opinion of the author, are left open to be addressed in future are:

- (i) Are electrochemical methods in conjunction with precise measurements of the isotope ratios for the constituent elements for compound synthesis capable of determining the stoichiometry of selected compounds with sufficient accuracy to produce at least a few standards for studies of their properties in relation to absolute deviations from stoichiometry? Would access to such standards make an impact on the understanding of process-induced changes in the point defect chemistry?
- (ii) How does Raman spectroscopy (including CARS) compare to and supplement reflectance spectroscopies in the real-time monitoring of heteroepitaxial processes?
- (iii) To what extent can nuclear methods, such as, PAC supplement ODEPR/ODENDOR in providing detailed information on the microscopic structure of defects in the III-V compounds and their II-IV-V<sub>2</sub> isoelectronic analogs?

#### **4. Control and Characterization of Stoichiometry-Property Relations for ZnGeP<sub>2</sub>**

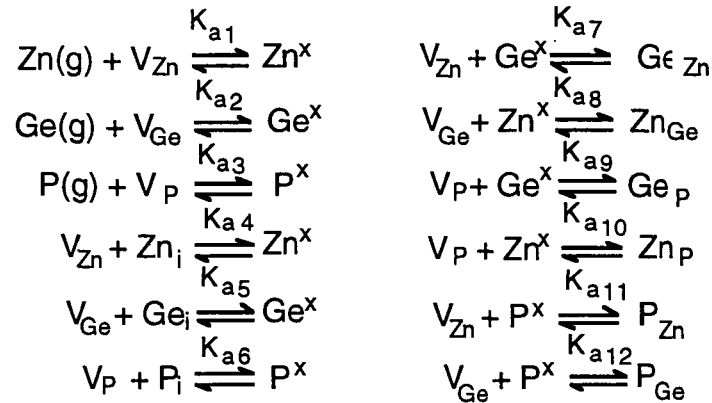
The chalcopyrite structure semiconductor ZnGeP<sub>2</sub> was chosen as an example for a more detailed evaluation because of the importance of native point defects in this material for its applications in non-linear optics, e.g., frequency mixing, harmonic generation and the generation of tunable infrared radiation by optical parametric oscillators (OPOs). In particular, residual absorption within the transparency range (0.67 to 13 μm) - due to native and extrinsic point defects - limits the performance and reliability of OPOs that are needed for monitoring of pollutants in the atmosphere and various other civilian and military applications. Two panel discussions were organized for the last day of the workshop addressing (A) the control of stoichiometry of ZnGeP<sub>2</sub> and (B) the assessment of the relation between point defects and linear optical properties in the transparency range. Since contemporary industrial and military applications of ZnGeP<sub>2</sub> are based on bulk single crystals and a comprehensive evaluation was intended the restriction on heterostructures was waived in this session. Dr. Verozubova of the Institute for Atmospheric Optics at Tomsk, Russia, set the stage for the deliberations of panel A by a detailed thorough review of stoichiometry control under the conditions of directional solidification, including synthesis of the compound from the elements, which is an integral part of producing ZnGeP<sub>2</sub> crystals with reproducible properties. The topic of compound synthesis was further elaborated by Dr. Tseybak of Inrad, Inc., at Northvale, NJ, USA, who identified fundamental problems related to the phase relations in the Zn-Ge-P system that are incompletely understood at present. A consensus was reached that the location of the maximum melting point in the Zn-Ge-P ternary composition field is probably not on the ZnP<sub>2</sub>-Ge pseudobinary, but its precise position is presently not known. As stressed by Prof. Rud' of the A.F. Ioffe Institut at St.

Petersburg, Russia, rectifying this deficiency and identifying the solidus shape and the relevant solidus-liquidus tie-lines is essential for progress in the fundamental understanding of  $\text{ZnGeP}_2$ . This point found general acceptance. Furthermore, Dr. Fiechter of the Hahn-Meitner Institut Berlin, Germany, presented the results of differential thermal analysis that reveal no evidence for the order - disorder transformation placed previously at  $950^\circ\text{C}$ , but suggest that this transition occurs at a temperature close to the melting point. Thus some of the early assessments of the phase diagram must be revised, adding additional urgency to a systematic reevaluation/extension of the set of thermodynamic data for this material. Dr. Vere of the Defense Research Agency Malvern, England, made an important contribution to the discussion by adding data on extrinsic impurities (e.g., Cu) that are either contained in the source materials or accidentally introduced during synthesis and growth and may directly or through complex formation affect the optical properties. Dr. Schunemann of Lockheed-Sanders at Nashua, NH, USA, focused onto the control of stoichiometry under the conditions of horizontal gradient freezing and on the fabrication of large single crystals with reproducible optical properties. Optimized melt stoichiometry, low thermal gradients, seeded growth along the phase-matching direction and transparent furnace design are the key to high process yield and the realization of high performance Ho-laser pumped OPOs. Prof. Bachmann of North Carolina State University, USA, established the link to the preceding focus of the workshop on heterostructures by a brief summary of the present state of heteroepitaxial growth of  $\text{ZnGeP}_2$  on GaP and Si substrates. In particular, organometallic chemical vapor deposition (OMCVD) provides for the growth of  $\text{ZnGeP}_2/\text{GaP}$  multiple heterostructures and  $\text{ZnSi}_x\text{Ge}_{1-x}\text{P}_2/\text{GaP}$  heterostructures with abrupt interfaces, as established by high resolution cross sectional TEM. In the context of the desired understanding and control of the point defect chemistry in  $\text{ZnGeP}_2$  an important result of OMCVD is the observation of a broad range of metastable solid solutions of Ge in the  $\text{ZnGeP}_2$  heteroepitaxial films that are produced below a minimum  $\text{Zn}(\text{CH}_3)_2:\text{GeH}_4$  flow rate ratio since it implies the incorporation of Ge into the lattice into both  $\text{Ge}_{\text{Zn}}$  and  $\text{Ge}_{\text{P}}$  antisite positions at a massive scale.

Prof. Rud' led the discussion of panel B by providing a comprehensive review of the history of research spanning the past 25 years on the properties of  $\text{ZnGeP}_2$  in relation to its native and extrinsic point defect chemistry, which he and his colleagues at the A.F. Yoffe Institute defined to a large extent<sup>2</sup>. The results of this research included the discovery of the optical brightening of  $\text{ZnGeP}_2$  upon low temperature annealing and pioneering work on electron irradiation-induced changes in the optical and electrical properties that provided important new insights. In particular, this work related the reduction of the near infrared absorption upon 2 MeV electron irradiation to a shift in the Fermi level associated with the formation of simple point defects, that is,  $V_{\text{P}}$ ,  $V_{\text{Zn}}$  and  $V_{\text{Ge}}$ . These point defects anneal out at  $600^\circ\text{C}$ , so that the stable initial p-type conductivity of the crystals must be related to more complex defects of presently not completely



understood chemical nature. Prof. Giles and Prof. Halliburton of West Virginia University at Morgantown, WV, USA, presented results of ESR, and ENDOR, evaluations of the crystals grown by Dr. Schunemann. The results of these studies show that, within the probed crystal volume, the dominant defects are singly ionized  $V_P^+$  donors and  $V_{Zn}^-$  acceptors. Of course, the vacancy defects are invariably connected to other types of defects, by chemical equilibria, that is:



which are characterized by equilibrium constants that are presently unknown. However, estimations of heats of formations - presented by Dr. Fiechter along the lines of Van Vechten's model - reveal considerable differences for antisite defects and vacancies. This implies that the temperature dependences of the equilibrium constants differ substantially so that the relative concentrations of defects change significantly as a function of temperature. In the opinion of the author, the interpretation of thermochemical treatments and of the defect chemistry under different growth conditions thus requires considerable caution and cannot be captured at present by a simple defect model. Prof. Dietz of North Carolina State University presented the results of time-dependent photoluminescence (PL) measurements on  $\text{ZnGeP}_2$  that determine the nature of the dominant radiative recombination as donor - acceptor (D-A) transitions. Also, he presented a model for the subbandgap absorption based on photoconductivity measurements that explain the optical brightening effect upon annealing as an effect of a shift of the Fermi level towards the mid-gap position. This is in accord with the preceding work of Prof. Rud' and coworkers on optical brightening and their interpretation of the changes in the near infrared absorption upon electron irradiation. Prof. Giles presented data on the photoluminescence for Dr. Schunemann's crystals, and attributed the PL to D-A transitions so that general agreement was reached on this particular point. The deep states that dominate the absorption and annealing behavior were associated by Prof. Giles with  $V_P - V_{Zn}$  pairing. However, photo-induced EPR probes a thin surface film while the optical brightening is a bulk effect. Therefore, alternative defect models cannot be excluded from consideration at the present time. Also, no consensus exists at present with regard to the interpretation of near-edge emission features that are observed for selected

processing conditions, e.g., for HPVT from a phosphorus and zinc supersaturated vapor phase. Theoretical predictions of the energy positions of the most important native defects relative to the band edges would be extremely helpful in settling some of the open questions. Dr. Fearn of Oxford University, England, presented initial results of tight binding calculations that hold much promise in this regard.

Questions that, in the opinion of the author, must be further evaluated in future are:

- (i) What are the tie lines between the liquidus and solidus surfaces of the Zn-Ge-P system that result in optimum crystal growth from the melt and what is the location of the maximum melting point in the ternary composition field?
- (ii) What are the equilibrium constants for the most important point defect equilibria among vacancy, interstitial and antisite defects and how do they shift with temperature?
- (ii) What are the energy eigenvalues for native defects in  $\text{ZnGeP}_2$  in the neutral and ionized states, what are the associated symmetries and how does this relate to the experimental results?
- (iii) What point defects contribute to the near edge emission observed for  $\text{ZnGeP}_2$  crystals?
- (iv) How do the shifts in absorption upon electron irradiation and annealing relate to the defect chemistry?

In summary, the discussions of this workshop addressed important questions regarding the control and characterization of stoichiometry at surfaces and interfaces and provided the forum for a detailed assessment of the understanding of one particular compound semiconductor, chosen to be  $\text{ZnGeP}_2$ . The participants expressed an interest in meeting again in 2-3 years to assess the progress in the field.

## References

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