About the D1 and D2 Dislocation Luminescence and Its Correlation with Oxygen Segregation

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Dedicated to Professor Dr. Wolfgang Schröter on the occasion of his 65th anniversary

It is well known that the dislocation luminescence (DL) in silicon consists of four main bands, conventionally labelled D1 to D4, where $E_1 = 0.807$ eV, $E_2 = 0.874$ eV, $E_3 = 0.95$ eV and $E_4 = 0.99$ eV, of which the D1 is considered of interest for optoelectronic devices working in the third window of optical communications. Although DL has been the subject of a number of investigations in the last twenty years, still some questions remain open, concerning both the origin of the dislocation luminescence and its intrinsic or extrinsic nature. We report in this paper the results of a combination of complementary dislocation generation processes (deformation and oxide segregation) and characterisation procedures (photoluminescence and surface photovoltage), which give a strong evidence that the D1 band is correlated in a very complex manner with the presence of optically active silicon self-interstitials and oxygen clusters.

1. Introduction

It is well known that dislocations in both Czochralski (Cz) and float zone (FZ) silicon emit light in the 0.8–1 eV range under optical or electrical excitation. The dislocation luminescence (DL) consists of a set of four main bands, conventionally labelled D1 to D4, with photon energies $E_1 = 0.807$ eV, $E_2 = 0.874$ eV, $E_3 = 0.95$ eV and $E_4 = 0.99$ eV. For a long time it has been agreed that a key characteristic of DL is insensitiveness of the energy position of the four bands on the dislocation generation procedure, which is also unaffected by the presence of metallic impurities, which, instead do influence the DL intensity.

Also the dislocation density (and the degree of deformation) strongly influences the intensity and the halfwidth of the different D bands in a very specific manner, with the D1 and D2 appearing only at high dislocation densities and with a broadening of D emission from sharp spectral lines to broad bands depending on the temperature and other unknown factors [1, 2]. Limiting our concern to D1 and D2 emission, none of the models reported in literature fit entirely with their very complex behaviour, considering also that at least the D1 band is the convolution of several sub-bands, as it has been shown by Ossipyan and coworkers [3] and that a band at 0.846 eV (D5 band), intermediate between D1 and D2, can be observed in certain circumstances, as in Er-doped dislocated samples [4].

Neither, there is an unambiguous consensus about the intrinsic or extrinsic nature of DL [3, 5–11].

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The D1 and D2 lines usually appear in heavily deformed FZ and Cz silicon samples as well as in the case of misfit dislocations in Si–Ge samples and their intensity increases with the deformation or with the increase of the dislocation density.

About the controversy on the origin of the D1 and D2 bands, Suezawa and Sumino [12] and Sekiguchi and Sumino [13] attributed these bands to Lomer-Cottrell dislocations and super-jogs originated by dislocation interaction. Shevchenko et al. [3, 5] concluded, instead, that they could come from dislocation defects, like kinks, jogs, short constrictions, without neglecting impurity states.

More recently, Jones and coworkers [14] suggested that the dislocation luminescence could be related to the presence of self-interstitial or vacancy clusters in the core of the dislocation, opening a new front in the dislocation luminescence controversy.

The effect of impurities on the DL intensity has been systematically proved by Higgs and coworkers [7, 8], who showed that the D1 and D2 luminescence appears only on slightly metallic impurity decorated dislocations in FZ silicon and showed also a straight dependence of DL intensity on transition metal contamination density. DL eventually disappears when metallic impurities segregate as silicides. The detailed mechanisms of the effect of impurities on electrical and optical properties is however not clear up to now, also because it is very difficult to prepare a truly clean (impurity free) dislocation array and contradictory evidences could be found in literature about impurity effects on DL [8–10].

We would like to remark, however, that the effect of oxygen on the dislocation photoluminescence itself and on the metallic impurity segregation in both FZ and Cz silicon has been so far underestimated. There, the conditions in fact occur for a 100% oxygen segregation at the dislocation core [15] followed by passivation of dislocation dangling bonds, after un-bonding of reconstructed bonds.

This process could occur in a wide range of temperatures, covering all the experimental conditions present in literature, as it would be also the case of misfit dislocations in CVD deposited Si/Si–Ge epilayers, where the oxygen concentration is even larger than in Cz silicon. In fact, oxygen has a strong binding at the dislocation core, which amounts to 1.2 eV for the monomer and 4.5 eV when it aggregates to a dimer [16, 17] compared to a maximum value of 0.87 eV for un-bonding [18].

Segregation of oxygen into the dislocation core could be possibly followed by a further reaction with metals exhibiting strong chemical affinity with oxygen, with the formation of O–Me bonds. The indirect evidence of metal oxide segregation in dislocated Er-doped silicon has been obtained by EXAFS measurements on dislocated Er-doped samples grown by Liquid Phase Epitaxy samples [19] on which the D5 line has been shown by PL measurements. This kind of evidence brings us to suppose that both oxygen and metals could be involved in the D1, D2 and D5 emission, at least in the case of metals exhibiting a strong affinity to oxygen. It should be also considered that oxygen increases the solubility of metals forming Me–O complexes in silicon, thereby depressing the formation of metal silicides [19], with favourable effect on the dislocation luminescence, which is quenched in the presence of metal silicides segregated at dislocations.

Our arguments about the oxygen involvement in the D1 and D2 luminescence are partially supported by a recent work of Tajima et al. [2], who submitted a dislocated Cz wafer to an oxygen nucleation and precipitation stage (450 °C, 64 h + 1000 °C, 16 h) and showed that the very broad D1 band detected at 0.81 eV in the temperature range

11–125 K shifts to 0.77 eV, with a 100-fold decrease in intensity, at 280 K. They, there-fore, suggest that this band (called D_b band) is the fingerprint of oxygen precipitates at dislocations and it is not traceable to D1/D2 luminescence. Some evidence of oxygen related luminescence has been also shown by Clays et al. [1] who observed that after an oxygen precipitation annealing, the D1 and D2 lines are clearly evident in the PL spectrum, whose intensity depends on the initial oxygen content. They, however, con-cluded that the dislocations nucleated at precipitates were responsible for the D1 and D2 bands at 0.807 and 0.874 eV.

As a possible conclusion, we could suppose that the "D1" band is the envelope of several bands, one of which comes from the contribution of silicon-oxygen species.

In order to prove this hypothesis, we supposed that if silicon oxide of an unknown stoichiometry segregated from supersaturated solutions of oxygen in silicon would be demonstrated to be luminescent, some correlation between "dislocation" luminescence and "oxygen" luminescence should be found.

To get insight into the problem we started recently a systematic work on the possible correlation between the photoluminescence features of intentionally dislocated Cz sili-con and of oxide precipitates in silicon. We report here some preliminary results of this work, which show some interesting, new aspects of the oxygen-related luminescence in silicon.

2. Experimental

Dislocated samples were prepared [20] starting from dislocation-free, B- and P-doped Cz grown 4″ diameter silicon wafers. The initial content of oxygen was 20 ppma.

Dislocation sources were nucleated first by scratching the surface of the samples along the ⟨011⟩ direction with a diamond tip loaded with 0.3 N weight. Then the sam-ples are elastically bent at room temperature in the cantilever mode along the transver-sal axis ⟨211⟩. Finally the samples are heated under stress for 1 h at $T = 650\,°C$ using a quartz and ultrapure graphite deformation apparatus in pure argon atmosphere. The temperature of 650 °C has been selected after having shown that in this condition the segregation of oxygen takes a minimum value [20], without excluding the possibility of oxygen passivation. Before any deformation and thermal annealing procedure, the sam-ples were submitted to the standard RCA cleaning procedure, to remove traces of me-tallic contaminants. It has been noted, in fact, that a broad band at about 0.77 eV is present in samples which are deformed or/and annealed without CP4 etch. The disloca-tion density was measured by etch pit count after Sirtl etch.

Oxygen segregated samples were extracted from a matrix of samples already system-atically studied using IR spectroscopy by Borghesi and Sassella [21]. The samples were prepared in VLSI conditions by MEMC Electronic Materials. We selected four samples (Cz62–65) typical for having had a short nucleation stage at 650 °C and a precipitate growth stage at 1000 °C of variable duration (see Table 1). All samples were subjected to a short preliminary dissolution treatment at 1000 °C to eliminate the grown-in precip-itates. The samples were characterised for oxygen losses using FTIR measurements and for the density of bulk micro-defects (oxide precipitates) by selective etching and opti-cal microscopy.

Minority carriers diffusion length measurements were carried out only on dislocated samples, using the standard SPV (Surface Photo Voltage) method, before and after the

Table 1

Parameters of the wafers used in the experimental matrix

sample	initial oxygen concentration (10^{17} cm^{-3})	dissolution treatment T (°C)/t (min)	nucleation T (°C)/t (h)	growth T (°C)/t (h)	bulk microdefects (10^{10} cm^{-3})
Cz62	7.28	1000/15	650/4	800/4 + 1000/4	0.92
Cz63	7.35	1000/15	650/4	800/4 + 1000/8	1.32
Cz64	7.38	1000/15	650/4	800/4 + 1000/16	1.64
Cz65	7.31	1000/15	650/4	800/4 + 1000/32	2.37

deformation, to check any effect of unintentional impurity contamination. The PL (photoluminescence) spectra were recorded with a spectral resolution of 3 nm, using standard lock-in techniques in conjunction with a grating monochromator and InGaAs as a detector. For the excitation, a quantum well laser ($\lambda = 808$ nm) was used. The power density was maintained constant at 6 W/cm^2 over all the samples examined, in order to make the comparison possible within the measured photoluminescence intensities, reported in arbitrary units (a.u.), coming from different samples.

The measurements were performed in a variable temperature cryostat in the temperature range 12–300 K.

3. Experimental Results

3.1 Dislocated samples

The results of diffusion length measurements at room temperature of reference samples (heat treated at the deformation temperature) and of plastically deformed samples are displayed in Table 2.

From this table one could conclude that the heat treatment without deformation (reference samples 1 and 2) does not influence the non-radiative recombination properties of the samples while deformation does, the decrease of L_d being proportional to the dislocation density N_d (cm^{-2}).

Thus, at room temperature, non-radiative recombination occurs at dislocations, inducing the observed temperature quenching of their photoluminescence (see below).

According to the model of Kittler and Seifert [22, 23], and Wilshaw et al. [24] the features of the temperature dependence of the recombination at dislocation are largely

Table 2

Effect of plastic deformation on the minority carriers diffusion length

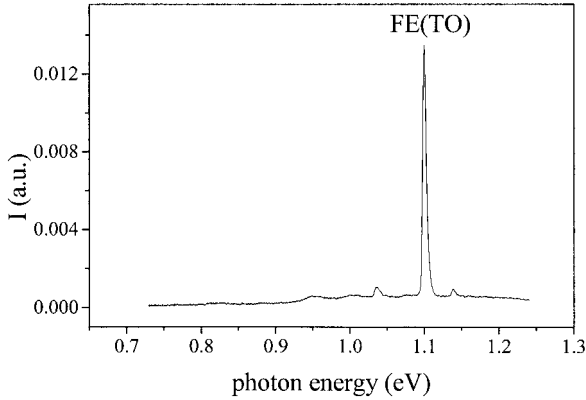| sample	L_d (as grown) (μm)	L_d (t.t. 670 °C) (μm)	N_d (cm^{-2})
ref. 1	240 ± 24	260 ± 26	–
ref. 2	380 ± 38	370 ± 37	–
D9-1-p	300 ± 30	220 ± 22	10^3
D8-1-P	230 ± 23	160 ± 16	10^4
D33-1-P	370 ± 37	60 ± 6	10^5
D39-1-P	390 ± 39	35 ± 3	$\geq 10^7$
D33-2-P	370 ± 37	50 ± 5	$\geq 10^7$

Fig. 1. PL spectrum ($T = 16$ K) of a dislocated sample ($N_d = 10^5$ cm^{-2})

depending on the trap level position with respect to the Fermi level, an increasing recombination with temperature coming from charged dislocations and deep dislocation centres.

In our case, the increase of the non-radiative recombination activity at increasing temperatures (from the temperature quenching of the luminescence) calls for the presence of a deep non-radiative recombination centre, possibly correlated with the C centre at $E_v + 0.35$ eV observed besides others by Cavalcoli et al. [25] with DLTS experiments.
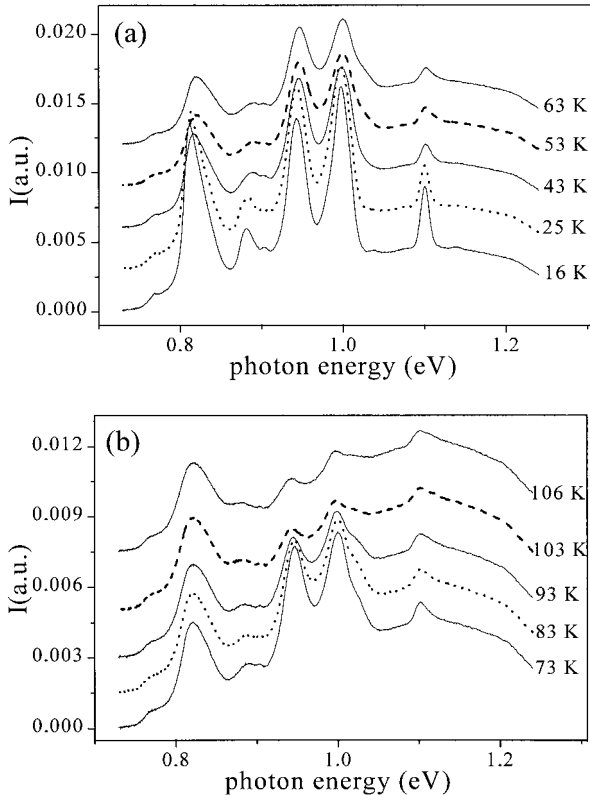
Fig. 2. PL spectrum of a dislocated sample ($N_d = 10^7$ cm^{-2}) at different temperatures

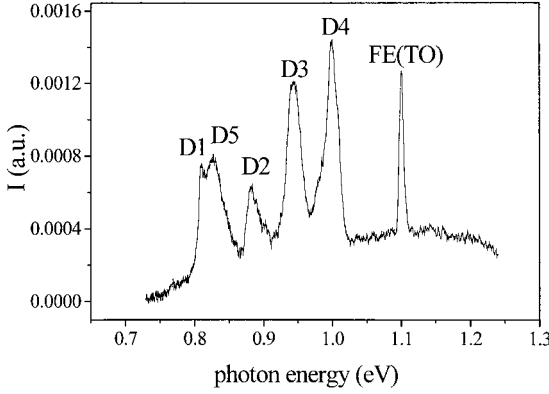Fig. 3. PL spectrum (T = 16 K) of a dislocated sample ($N_d = 10^8$ cm^{-2})

The results of photoluminescence measurements are reported in Figs. 1 to 3. From Figs. 1 to 3 one could observe that the full spectrum of dislocation luminescence is developed only when $N_d \geq 10^7$ cm^{-2}, while a new line (D5, with E = 0.826 eV at 16 K) emerges at $N_d = 10^8$ cm^{-2} (see Fig. 3).

Figures 2a and b, moreover, show that a progressive quenching of the D bands luminescence occurs at increasing measurement temperature, with the simultaneous shift of the D1 band position.

From Fig. 4, which reports in detail the temperature evolution of the peak energy of the D1 line with the temperature for the sample D39-1-P ($N_d = 10^7$ cm^{-2}), one eventually observes that the gradual shift of the position of the D1 line towards higher energies peaks to a maximum at about 0.825 eV (T = 125 K).

We remind here that the experimental temperature dependence of the intensity I of the D4 and D3 PL bands was shown [20] to be fitted using the Kveder's model [6], which assumes that the emission is associated to a recombination process between two levels of a defect centre, using the following equation:

$$I = \frac{B}{1 + C_e T^{3/2} \exp\left(-E_1/kT\right)} + \frac{B}{1 + C_h T^{3/2} \exp\left(-E_2/kT\right)} , \qquad (1)$$

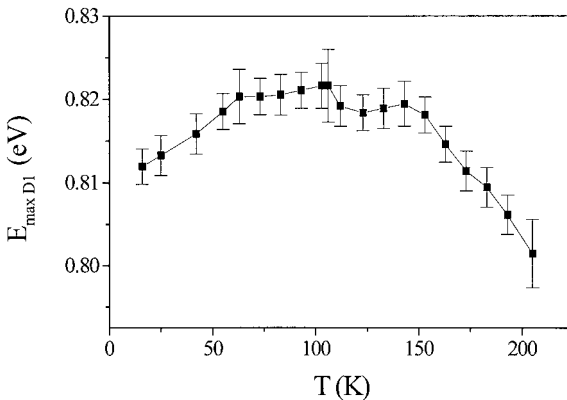

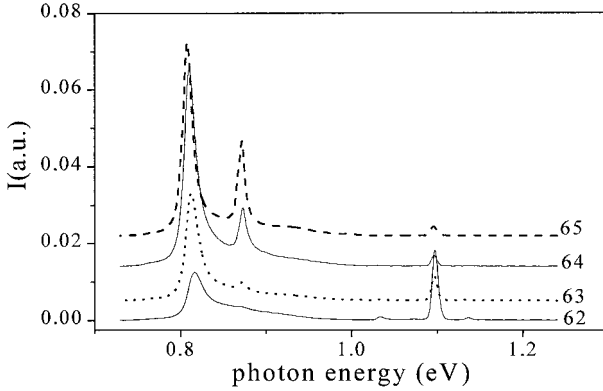Fig. 4. Temperature dependence of the D1 band of a dislocated sample ($N_d = 10^7$ cm^{-2})

Fig. 5. PL spectra ($T = 12$ K) of the Cz62–65 samples

from which the values of 0.07 eV and 0.034 eV were obtained for the energy levels associated to the radiative recombination channel responsible of both the D3 and D4 band [20], the D3 line being the phonon replica of the D4 one.

This model was instead unable to give results of full physical meaning in the case of both the D1 and D2 lines [20], possibly because of the simultaneous occurrence of a radiative and non-radiative recombination process at different centres, in good agreement with the arguments given above, about the presence of a deep DLTS active recombination centre.

3.2 Oxygen precipitated samples

The results of PL measurements on precipitated oxygen samples are reported in Fig. 5, which only shows the typical signatures of the D1 and D2 bands, in addition to the band to band recombination, with intensities which increase for both lines with the duration of the growth cycle at 1000 °C, and therefore with the size of the precipitates.

Moreover, the intensities of the D1 and D2 lines of the sample 64, precipitation annealed for 16 h at 1000 °C, measured at 12 K, is of a factor five larger than the intensities of the same lines measured in dislocated samples.

Apparently, the D2 line emerges from the shoulder of the D1 line only at precipitation annealing stages longer than 8 h (see Table 1). The very flat and low background
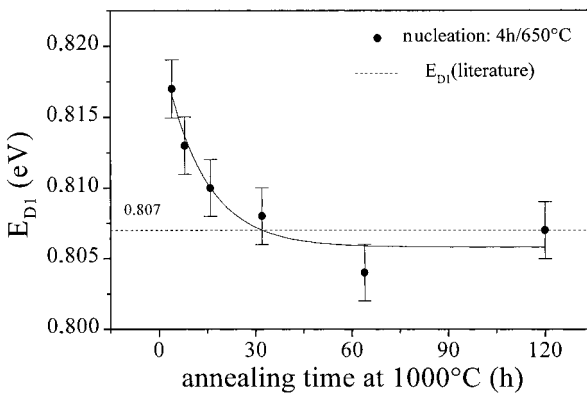

Fig. 6. Shift of the position of the D1 band as a function of the growth annealing duration at 1000 °C (time in hours)

in the 1–1.2 eV range could be taken as a fingerprint of the very good quality of the substrate.

When the peak position of the D1 line is plotted as a function of the annealing time at 1000 °C (see Fig. 6) one can observe a systematic evolution of the peak position from energies well above the conventional value assigned to the D1 line (0.807 eV), which is asymptotically reached after more than 120 h. Incidentally, TEM investigations of the whole matrix of oxygen segregated samples [26] indicated the presence of dislocation loops around the oxygen precipitates as soon as the PL emission of the D1 line reaches is asymptotic value at 0.807 eV.

4. Discussion and Conclusion

Even a preliminary, qualitative analysis of these results shows that a correlation exists among "oxygen" and dislocation luminescence in silicon, as both kinds of extended defects give rise to the D1 and D2 band luminescence, oxygen precipitates behaving, however, as much more efficient light emission sources.

In fact, the D1 luminescence becomes detectable only in plastically deformed samples presenting a dislocation density in excess of $10^7 \, \mathrm{cm}^{-2}$, as it would be due to localised emission at centres resulting from dislocation interaction or intersections. The "oxygen" luminescence of the oxygen segregated sample Cz62 of Table 1, with a bulk microdefect density of $9 \times 10^9 \, \mathrm{cm}^{-3}$, or $4 \times 10^6 \, \mathrm{cm}^{-2}$, instead, is a factor of five more intense than that of a dislocated sample having the same area density of luminescence centres (D39-1-P of Table 2).

Concerning the "oxygen precipitates" luminescence, it is to be noted that the isothermal shift of the D1 energy with the oxygen precipitation time, and then, with the oxide precipitates size, seems to follow the progress of a dislocation nucleation process from a growing oxide precipitate, which while growing injects silicon self-interstitials in the silicon matrix, according to the exigent volume model of Hu [27] and Tan [28]. The D1 luminescence might therefore be associated to dislocation precursors, more than to the dislocations themselves.

More insight into the problem can be obtained by displaying in Fig. 7, in addition to the data about the temperature dependence of the position of the D1 band of our dislocated samples (see Fig. 4), the saturation values of the D1 band in oxygen precipitates samples, the results for the D_b band obtained by Tajima [2] in high temperature
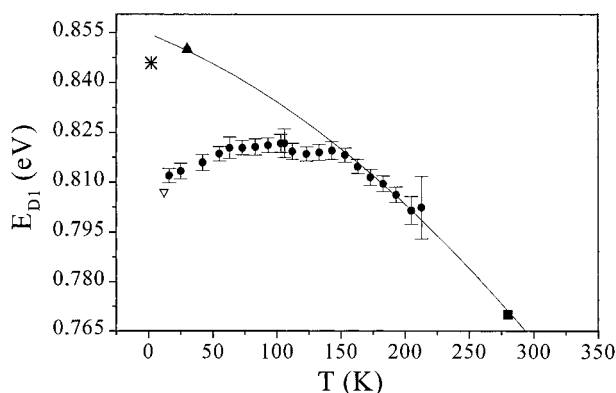
Fig. 7. Temperature dependence of the energy position of the D1/D5 line of several oxygen segregated and dislocated samples (✳ Ref. [4]; ■ Ref. [2]; ▲ Ref. [29]; ▽ this work, oxygen segregated sample; ● this work, dislocated samples)

oxygen segregated samples (E_b = 0.77 eV at 280 K), those reported by Steinman and Grimmeiss [29] in dislocated silicon annealed at 450 °C (a band at 0.85 eV at 30 K) and those for the D5 band of dislocated Er-doped samples (0.846 eV at 2 K) [4].

Apparently, the luminescence of plastically deformed samples submitted to a high temperature or oxygen precipitation annealing, or decorated with oxygen precipitates (Er-doped sample) follow a quite similar behaviour (solid line of Fig. 7), which is the fingerprint of a centre associated to some kind of oxygen segregation at dislocations and responsible of the "D5-D$_b$" emission.

The D1 band luminescence of dislocated samples, which were plastically deformed in a range of temperature where the oxygen segregation takes a minimum value, as well as the oxygen segregated samples, follows instead a different behaviour at low temperature, which could be interpreted as a shift of the emission intensity of the D1 band towards that of the D5-D$_b$ band at increasing temperature. The "D1" band is, therefore, the convolution of two lines, of which one, persisting at high temperatures, is related to oxide decorated dislocations, the other to dislocation precursors or to clusters of self-interstitials in the dislocation core, which is more intense at low temperatures.

The D1 dislocation emission could be therefore depicted as due to a matrix of inter-connected "clean" (D1 emitting) and oxygen decorated (D5 emitting) dislocations, of which the "clean" ones are most efficient radiative recombination centres at low temperatures. Here, "clean" takes only the meaning of dislocations or dislocation precursors free of oxygen precipitates, as we cannot exclude some effect of metallic contamination.

In conclusion, we were able to show that in Cz silicon the luminescence in the range of the "D1" emission arises from "clean" and oxygen decorated dislocations, and that it is possible also to follow the dislocation nucleation from the aggregation of self-interstitials injected in the bulk from growing oxide precipitates.

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