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# Self-organized formation of erbium-silicon-oxide superlattice

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A self-organized Er-Si-O superlattice, in which the Er-O octahedron is assembled, has been demonstrated. The Er-Si-O superlattice is formed by coating a Si(100) substrate with an $ErCl_3$/ethanol solution, followed by rapid thermal oxidation and annealing. The single crystalline nature gives hyperfine structures in photoluminescence spectra. Room-temperature Er-related 1.53 μm photoluminescence is observed with a peak line width as small as 4 meV. The superlattice can be excited directly into the Er intra-4*f* states, or indirectly, through photocarriers. Er concentrations as high as 14 at.% are achieved, incorporated in a crystalline superlattice with a 0.9 nm periodicity.

Key words: self-organization, silicon, erbium, superlattice, photoluminescence

## 1. INTRODUCTION

Intense 1.5 μm emission originating from the intra-4*f* shell transitions in $Er^{3+}$ ions has been attracting much attentions to the applications to light sources for optical communication systems[1]. Looking into the future, erbium doping into silicon and the related materials has been strived to obtain the Er-related intense emission at room temperature in order to realize Si-based optoelectronic integrations[2,3]. Nowadays it has been shown the validity of oxygen incorporating to enhance the Er-related emission and improve the thermal quenching[2,3], and a stimulated emission at 1540 nm from erbium and oxygen co-doped nanocrystalline silicon has been demonstrated at room temperature[4].

In this paper, we present self-organization of Er-Si-O superlattice on silicon substrates by a simple and successful process, and striking results of room temperature photoluminescence (PL) measurements for the Er-Si-O superlattice originated from the single crystalline nature.

## 2. EXPERIMENT

A single crystal Czochralski-grown n-type silicon (100) wafer (P-doped, resistivity : 5 Ωcm) etched in a 5% HF solution was used. Er-Si-O complexes on Si surface are formed by a spin-coating process (3000 rpm for 1min) with an $ErCl_3$/ethanol solution, followed by the following two-step annealing process, rapid thermal oxidization (RTO) and annealing (RTA) processes. The $ErCl_3$ solution was obtained by dilution of a saturated $ErCl_3$/ethanol solution with ethanol to 10 times. Total amount of erbium on a planer Si surface after the coating process is estimated about $3 \times 10^{15}$ $cm^{-2}$ by a Rutherford backscattering spectrometry (RBS). The combined thermal process with RTO and RTA (RTOA) is performed continuously with a short interval by using a rapid thermal annealing system, and by switching of the ambient flow gases between oxygen for RTO and argon for RTA at 1 atm. RTO and RTA processes were carried out typically at 900°C for 4 min and at 1200°C for 3 min respectively. The waiting time to exchange the ambient from RTO to RTA is 3min under gas cooling. Temperature in the waiting time decreases below 500°C for 10s after the RTO-heating off. In this experiment, an RTO sample was also fabricated for comparison.

RTOA and RTO samples were analyzed using Rutherford backscattering spectrometry (RBS) using 2 MeV $He^+$ beam at a scattering angle of 165°. Photoluminescence (PL) are performed at room temperature by using various lines of an argon ion laser. The nominal laser power was 100 mW. The PL emissions were monitored through a 48 cm monochromator by a liquid-nitrogen cooled Ge detector and recorded with a lock-in amplifier.

## 3. RESULTS

Figure 1 shows RBS channeling spectra of RTO and RTOA samples. The spectrum of a Si single crystal (c-Si) is also shown by a dashed line for comparison. In RTO sample, the surface peaks of erbium, oxygen and silicon atoms, which widths are comparable to the system resolution, have been observed. Due to the oxidation, the surface peak yield of silicon becomes larger than

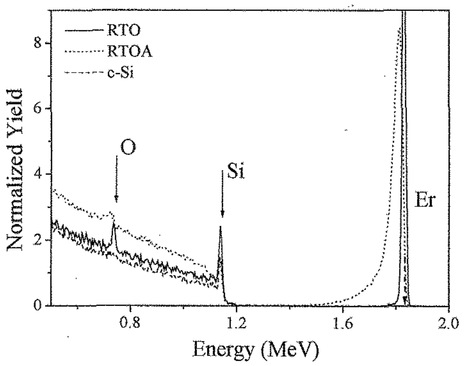


Fig.1 RBS channeling spectra of RTO (solid line), RTOA (dotted line), and c-Si (dashed line) samples. Channeling was performed in the [100] direction. The arrows indicate the surface channels for Er, Si, and O.

that for c-Si. The Si part of the channeling spectrum for RTO sample shows no difference when compared to that for c-Si. It is shown that the RTO process does not modify the channeling profile for Si but forms an Er-Si-O thin layer at the surface. Assuming an $Er_2O_3$-$SiO_2$ mixture structure as the Er-Si-O matrix, the layer thickness can be estimated about 4 nm from the peak yields. After the following RTA process, erbium and oxygen atoms are redistributed into the depth. In contrast, the surface peak yield of silicon becomes smaller but the peak profile remains. The decreasing of the yield of silicon suggests decomposition of Si-O bonding due to the following RTA process. The profile of erbium and oxygen for RTOA sample shows similar behavior. The atomic fractions of erbium and oxygen are 0.02 and 0.08 at the surface and decrease exponentially into the depth.

Figure 2 shows TEM bright field micrograph of RTOA sample, with the cross sectional view (a) and the surface tilted 43° away from the edge-on position (b). The images reveal discrete islands on the specimen surface, with sizes between 30 and 400 nm, and with a height between 20 and 120 nm. The surface coverage is about 15%. A tension can be recognized from the bending contours close to the island in the substrate, and is probably caused by a tendency of the islands to grow coherent on the substrate. Energy dispersive spectroscopy (EDS) analysis revealed that the islands contain erbium, silicon and oxygen. However no EDS signal of erbium was observed in the substrate. It is suggested that the Si-O bond breaking and the clustering proceeds during RTOA process and finally the Er-Si-O islands are formed. The exponential decrease of erbium in the RBS signal can be understood from the micro structural observations as the result of an average over the film with Er-Si-O islands on a rough Si substrate. Composition of the island can roughly estimated Er:Si:O = 1:2:4 by the RBS yields and the surface coverage of Er-Si-O island.

Figure 3 shows a cross sectional view TEM image of an Er-Si-O island (a), (b) and the selected-area electron diffraction pattern (c). The single crystalline Er-Si-O pattern is identified by the diffraction pattern. The TEM image revealed self-organization of the superlattice structure with 0.9 nm period. From the diffraction pattern, the d-spacings and the angle are estimated to be 0.868, 0.304 nm and 83°, and the crystalline system is expected to be monoclinic system. So far two families of Er-Si-O crystalline systems, $Er_2Si_2O_7$ and $Er_2SiO_5$, have been reported in the JCPDS-files[5]. These erbium silicates can have several crystalline structures determined by the phase diagram, however the Er-Si-O superlattice could not be identified as one of the known compounds in the JCPDS-files.

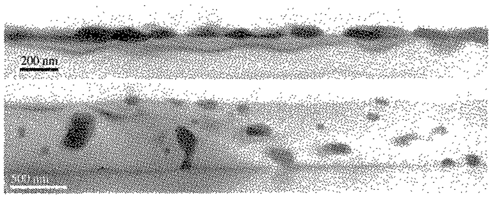
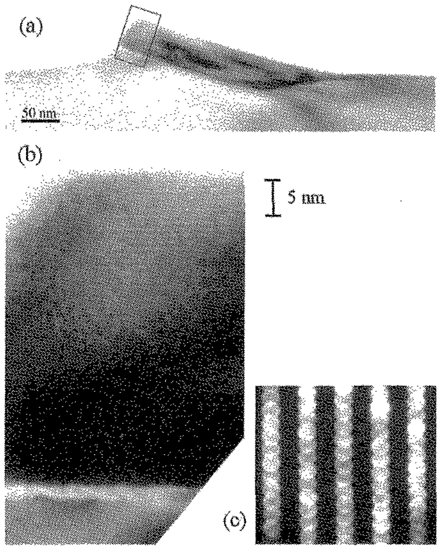


Fig.2 TEM bright-field micrographs of the RTOA sample in cross-sectional view (a), and with the surface tilted 43° away from edge-on position (b). Nanoscale Er-Si-O complexes have formed on the Si(100) substrate.



Fgi.3. TEM BF images of a Er-Si-O island on a Si (100) substrate ((a), (b)), and the selected-area electron diffraction (SADP) pattern of Er-Si-O complex (c). The d-spacings and the angle are estimated to be 0.868 x 0.304 nm and 83°.

Figure 4 shows the PL spectra excited by either 488.0 or 476.5 nm line of the Ar ion laser at room temperature for (a) RTOA and (b) RTO samples. Each excitation wavelength corresponds to the resonance condition of the transition in Er ions (488.0 nm) and the non-resonance condition (476.5 nm). Excitation mechanism under the non-resonance condition is energy transfer of electron-hole pair recombination energy from the host material. Under the 488.0 nm excitation, a sharp peak at 1.53 μm centered in an emission band between 1.45 and 1.6 μm is shown in the each sample, which is originated from the intra-4f-shell transition from the first excited state ($^4I_{13/2}$) to the ground state ($^4I_{15/2}$) in $Er^{3+}$ ions. For the RTO sample under the 476.5 nm excitation, a small peak located at 1.53 μm is clearly seen. However, the RTOA sample shows an intense peak at 1.53 μm under the 476.5 nm excitation, and the peak intensity is higher than that of the RTO sample under the 488.0 nm excitation. Due to the following RTA process, the PL emission located around 1.53 μm is enhanced about five times while the peak position remains unchanged.

On the other hand, the emissions relative to the host material show the particular behavior due to the following RTA process as shown in Fig.3. The PL spectra have three broadband emissions around 1.0, 1.15 and 1.2 μm at the least, which are independent of the excitation wavelength. The emission around 1 μm can be also observed in the RTO sample as a higher energy tail below 0.9 μm. The emissions below Si band gap are originated from the donor impurities (1.15 μm) and the deep levels (1.2 μm) in Si, and the intensities are reduced by the RTA process. In contrast, the emission band around 1 μm is grown about five times by the following RTA and the value almost agrees with the enhancement of the 1.53 μm emission intensity. It is suggested that the outgrowth is responsible for the enhancement of the 1.53 μm emission as the host material. The origin of this broad emission band has not been identified but it is considered to be due to certain transitions in Er-Si-O matrix formed by the RTOA process.

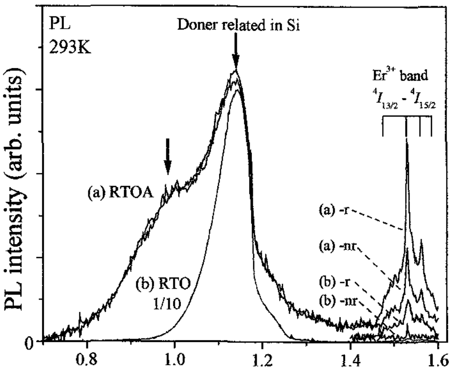


Fig.4 PL spectra of RTOA (a) and RTO (b) samples at room temperature, measured under excitation at either 488.0 (r) or 476.5 (nr) nm. The pump wavelengths are indicated near the graphs.

Figure 5 shows typical Er-related PL spectra of the RTOA sample, observed under the 488.0 and 467.5 nm excitations at room temperature. Then the resolution is 3 nm, and the intensities are normalized by the peak value. A sharp intense PL peak at 1.529 μm (photon energy of 0.811 eV) with a full width at half maximum of 4.0 meV and a sub-peak at 1.562 μm (photon energy of 0.794 eV) are observed at room temperature. The intensity ratio of the three peaks, indicated by arrowheads in the figure (1.529, 1.562 and 1.586 μm), is independent of the measurement conditions and the RTOA process conditions. The spectra for the each excitation condition are quite the same shape. An agreement with the PL fine structures between the direct and the indirect excitations means that both of the PL peak emissions come from the same kind of $Er^{3+}$ ions. This indicates a possibility of controlling the excited states both electrically and optically.

## 4. DISCUSSIONS

The following RTA process up to 1100°C is less effective to optical activation of erbium ions, and the Er-related PL intensity drastically increases at the RTA temperature above 1200°C. This behavior is shown in various RTO samples with the oxidation temperature range from 900°C

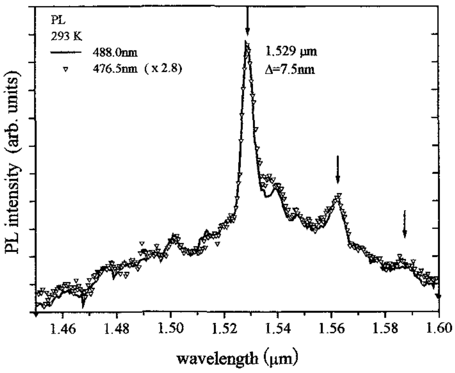


Fig.5 Room temperature PL spectra of the RTOA sample excited by 488.0 or 476.5 nm lines of an argon ion laser. The arrows indicate transitions between different Stark levels.

to 1000°C for a few minutes. It is likely that the self-organization rapidly proceed due to breaking of the Si-O network. Considering the lower decomposition temperature of $ErCl_3$ (below 800°C) and the higher melting point of $Er_2O_3$ (about 2300°C) than the RTOA process temperature, Er-O bonding is formed preferentially by RTO process, and still remains during the following RTA process in spite of the Si-O bond breaking. We expect that the Er-O complexes formed by RTO, as they are, are self-organized together with silicon, and the formed Er-Si-O matrices become optically active by the following RTA. The speculation is also supported by the RBS result for RTOA sample, which the profiles of erbium and oxygen atoms show similar behavior.

RTOA process is considered to be a condition comparatively similar to thermal equilibrium. It is speculated that the majority of luminescent erbium ions is arranged at the specific steady site by the thermal equilibrium processes, so that the inhomogeneous broadening is suppressed. A striking feature of the room temperature PL is the narrow line width of 4 meV. The line width is comparable with a homogeneous linewidth of erbium ions extracted from inhomogeneous broadening of various Er-doped glasses[6]. So far room temperature PL emissions of erbium ions have been observed in several Er-doped Si related materials[2-4], however the PL spectra show inhomogeneous broadening. Their luminescent centers are considered to be in inhomogeneous medium because of the formation by using thermal non-equilibrium. The PL spectrum fine structure also shows crystalline-field splitting of the $^4I_{15/2}$ manifold in $Er^{3+}$ ions due to the local environment of $Er^{3+}$ ions. The emission peaks corresponding to Stark levels of the $^4I_{15/2}$ manifold in $Er^{3+}$ ions are indicated by allows in Fig.2. From comparison among Stark level energies of the $^4I_{15/2}$ manifold measured in several Er-related materials, the splitting behavior is good agreement with those of $Y_2SiO_5$:Er [7] and $Er_2O_3$ [8] crystalline compounds which are with a sixfold coordination around Er of oxygen atoms Er-$O_6$. Details of the Stark splitting have discussed elsewhere[9]. More research is required to determine the atomic-scale structure of the Er-Si-O layered structure observed in this work. We speculate that a self-assembly process leads to the formation of Er-$O_6$ octahedra that order in a layered structure. Indeed, self-assembled layers of Er-$O_6$ octahedra in erbium disilicates made by using the Verneuil method and oxide sintering of $Er_2O_3$ and $SiO_2$ have been observed before[10]. In such a Er-Si-O superlattice, the Er-$O_6$ octahedra may then be separated by Si rich layers that act as sensitizers for the Er. Quantum confinement in these thin Si-rich layers would then lead to the blue-shift as observed in the PL emission band of Fig.4. Further study to determine the crystalline structure now goes on.

## 4. CONCLUSION

We have demonstrated the self-organization of the luminescent Er-Si-O superlattice on silicon surface, and the sharp and efficient PL emission from erbium ions at room temperature. It is shown that the luminescent Er-Si-O superlattice with high erbium concentration about 14% are formed by RTOA. We conclude that RTO acts as a pre-formation process of the Er-O luminescent center, and the following RTA do as processes for reformation of the effective host material and activation of the luminescent center. The PL spectra show the fine structure with a homogeneous linewidth (4 meV), and the crystalline-field splitting of 4f electron in Er3+ ions has been observed. Then the Er-related PL spectra are independent of the excitation mechanism. The simple and productive process promises the application to the silicon optoelectronics integration.

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