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Size-controlled Si nanocrystals fabricated by electron beam evaporation

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Multilayers consisting of silicon nanocrystals (Si NCs) and SiO₂ have been successfully fabricated by electron beam evaporation, using pure Si and SiO₂ targets in an oxygen-rich atmosphere for alternately depositing silicon-rich oxide (SRO) layers and SiO₂ barriers, respectively. A post-deposition annealing process was carried out at different temperatures in order to achieve the Si precipitation in the form of nanocrystals. The stoichiometry of the layers was determined by X-ray spectroscopy, which confirmed the controlled silicon oxidation in order to attain SRO layers. Transmission electron microscopy and Raman-scattering measurements confirmed the presence of crystalline Si-nanoprecipitates. Photoluminescence spectra from the Si NC samples could be deconvolved into two contributions, whose dynamics suggests that two different luminescent centres are responsible for the optical emission of the samples.

1. Introduction

Since the middle of the last century, silicon has been one of the most important semiconductor materials studied by researchers thanks to its abundance, non-toxicity and good electrical properties, thus being widely employed in the electronics industry. However, its indirect band gap is the main drawback for optical applications, which drastically decreases the probability of electron-hole radiative recombination. As it is well known, nanostructuring Si results in the quantization and energy increase of its allowed electronic states, properties that strongly depend on the nanostructure size.^[1–3] The consequent tunability of the band gap of Si nanocrystals (Si NCs) has been widely investigated in order to employ their optical properties in light-emitting,^[4–7] photovoltaic^[8–10] devices or memory applications.^[11,12] Matrix-embedded Si NCs are one of the most employed configurations, being SiO₂ the most usual dielectric matrix. By controlling the stoichiometry of silicon oxide (i.e., the Si excess), a high-temperature annealing process can be carried out which promotes the precipitation of the Si excess in the form of Si NCs.

On one hand, the control of the Si NC size has been achieved by the Si NCs/SiO₂ multilayers (MLs) approach, where the stoichiometric SiO₂ layers play the role of barrier against Si diffusion, thus limiting the growth of the Si NCs along the vertical direction.^[1] In addition, several works on the effect of the annealing temperature (T_a) and the thickness of the SiO₂ barriers have been carried out to determine the optimal structure for optoelectronics applications.^[13,14] On the other hand, the fabrication of these nanostructures has basically been achieved by means of either chemical-vapor deposition,^[3,15] sputtering,^[16] or Si implantation in SiO₂.^[17] The electron-beam evaporation (EBE) technique has also been employed to generate multilayered Si NCs/SiO₂ structures. However, whereas the SiO₂ layers can be easily EBE-deposited, the silicon-rich oxide (SRO) layers are typically achieved via either thermal

evaporation^[18] or EBE^[19] of SiO targets. So far, the possibility to fabricate Si NCs evaporating both SiO₂ and SRO layers employing the same EBE technique has not been explored yet. In the case of SRO, using pure Si target provides an alternative technique-compatible strategy; indeed, this has proved useful to synthesize colloidal Si NCs by placing the pure Si target in deionized water, followed by a thermal treatment via ultra-short pulsed laser ablation.^[20]

In this work, we present the fabrication, entirely carried out by means of the EBE technique, as well as the structural and optical characterization of Si NCs embedded in a SiO₂ matrix. For this, a ML approach was employed by alternating the deposition of SRO layers and SiO₂ barriers, respectively using pure Si and SiO₂ targets in an oxygen-rich atmosphere.

2. Results and discussion

First, we study the stoichiometry of SiO₂ and SRO layers deposited by e-beam and annealed at 1200 °C by X-ray photoelectron spectroscopy (XPS). For this analysis, due to the limited depth resolution of the experimental set-up (during the sputtering process), bulk SiO₂ and SRO samples were employed for determining their composition, and thus the equivalent on of the ML samples. Figure 1 shows the Si2p and O1s XPS signals, whose areas under the curve were determined and corrected for the sensitivity factor of each atomic specimen. From this analysis, atomic concentrations of Si (34%) and O (66%) were determined for the SiO₂ sample, which confirms its stoichiometry. In contrast, the SRO layer presents a clear substoichiometry with atomic values of Si (42%) and O (58%), corresponding to SiO_{1.4}, which confirms that Si is partially oxidized when it is evaporated from a pure Si target with an O₂ line. Exploring in more detail the Si2p spectra of both SiO₂ and SRO layers, deconvolution via different pseudo-Voigt fits was performed in order to determine the contribution of the different oxidation states of Si. In the case of the SiO₂ sample [see Figure 1(a)], the main contribution corresponds to the Si⁴⁺ state (103.7 eV), with a decreasing contribution of the

other oxidation states as the oxidation number decreases, namely Si^{3+} (102.6 eV), Si^{2+} (101.4 eV) and Si^{1+} (100.1 eV), progressively. No contribution of Si^0 is observed, which is in agreement with the stoichiometry of this layer. On the other hand, Figure 1(b) shows the $\text{Si}2p$ signal of the SRO layer, exhibiting a broader spectrum than the SiO_2 layer. In this case, the distribution of the different oxidation states of silicon is clearly changed, decreasing the Si^{4+} (103.7 eV) contribution and increasing the Si^{3+} (102.5 eV), Si^{2+} (101.3 eV) and Si^{1+} (100.0 eV) ones. In contrast to the SiO_2 layer, the SRO layer shows the metallic Si^0 (98.6 eV) contribution, indicating Si-Si bonds due to the lack of oxygen. Regarding the O1s analysis of the SiO_2 presented in Figure 1(c), a single pseudo-Voigt function was fitted at 532.0 eV, indicating that oxygen is only bound to Si atoms in a single configuration (-O-). However, the SRO layer exhibits an O1s broader spectrum [see Figure 1(d)], which suggests that part of the oxygen presents different bonds. The main contribution is centered at 532.1 eV and it is again attributed to oxygen bound to Si atoms in single configuration (-O-), like within the SiO_2 layer. The other contribution displays a higher energy (533.6 eV) and it can be directly correlated with the substoichiometry of the layer. In this case, peroxy configuration (-O-O-) is sensitive to be formed in the regions where Si excess is present.^[21] In Table I, the binding energy, integrated area and resulting atomic concentration of each contribution are summarized.

Transmission electron microscopy (TEM) images of the test sample annealed at 1200 °C were analyzed in order to match the nominal thicknesses with the measured Si NC sizes. In the Figure 2(a), an energy-filtered TEM (EFTEM) image of this sample is exhibited, filtering the energy around the Si plasmon peak (~17 eV). The image clearly confirms the ML structure even at this high annealing temperature, where the brightest zones correspond to a higher Si concentration. In the stack near the Si substrate (the first layers at the bottom of the image), the SiO_2 barriers are kept constant at a measured thickness of 2.7 nm, while the measured

thickness of the SRO layers varies from 3.5 nm to 4.7 nm. In the second stack (layers at the top of the image), the SiO₂ barriers exhibit thickness values that vary from 2.3 nm to 3.5 nm, with constant SRO layers of a measured thickness of 3.5 nm. Thanks to this test sample, nominal and real thicknesses were correlated. Indeed, the increase in nominal thickness clearly corresponds to an increase in the real (measured) thickness. This relation between nominal and measured SiO₂ and SRO thicknesses is plotted in Figure 2(b), displaying a linear trend. This study has allowed calibrating our deposition set-up and determining the real thickness of the SRO layers (L_{SRO}). High-resolution TEM (HRTEM) images were also acquired in the center of this first stack to determine whether Si NC formation was achieved during the annealing process. In Figure 2(c), different Si lattice planes (highlighted by red lines) are observed and attributed to the Si NC formation, providing an unequivocal proof that the Si nanoaggregates contain a non-negligible crystalline phase. It is important to note that only crystalline planes parallel to the electron-beam can be observed, which substantially reduces the number of visible Si NCs.

Raman measurements were performed at room temperature on samples deposited on fused silica substrates. In Figure 3(a), the Raman spectra corresponding to the sample with the largest SRO thickness ($L_{\text{SRO}} = 4.7$ nm), annealed at different T_{a} , are plotted. Two different features can be clearly distinguished from the spectra: a broad band from 300 cm⁻¹ to 500 cm⁻¹, with its maximum around 470 cm⁻¹, related to disorder-activated acoustical and optical modes in amorphous Si and amorphous SiO₂, and a peak centered around ~517 cm⁻¹, attributed to the crystalline Si transversal-longitudinal optical (TO-LO) phonon mode. The first band is observed in all the spectra, whereas the crystalline feature appears only after an annealing beyond 1000 °C. This last feature indicates the formation of crystalline aggregates under these particular thermal annealing conditions. Despite the fact that the precipitation of the Si excess within the SRO layers and the formation of amorphous Si nanoclusters already

takes place at temperatures as low as 700–800 °C, a higher T_a is necessary for the crystallization of these nanoaggregates.^[13,22] In this regard, the presence of the crystalline Si peak in the spectra corresponding to samples annealed at $T_a > 1000$ °C confirms the presence of a Si crystalline phase, which totally agrees with the lattice planes observed by HRTEM [see Figure 2(c)].

The Raman spectra from the samples annealed at 1200 °C and containing different L_{SRO} are displayed in Figure 3(b), showing the above-mentioned contributions. However, in this case, the peak related to crystalline Si is only observed for L_{SRO} equal or thicker than 4.3 nm, with no observation of thinner SRO layers. In fact, the observed contribution from the SiO₂, either coming from the surroundings or from the substrate, could be masking the crystalline contribution. Another possible explanation might be ascribed to the fact that a critical Si mass is necessary to achieve the formation of crystalline aggregates.^[23] Analyzing this crystalline feature using the phonon confinement model described in Ref. 24 in samples with $L_{\text{SRO}} = 4.3$ nm and $L_{\text{SRO}} = 4.7$ nm [see Figure 3(b)], we have found a crystalline Si NC size of 3.9 and 4.2 nm, respectively. In addition, by comparing the total Si-cluster size from TEM and the Si-crystalline size from the Raman analysis, we conclude that there is an almost full crystallization of the precipitated Si, in good accordance with previous results in a similar system.^[24] These results are in excellent agreement with HRTEM images, where crystalline nanoaggregates are observed with sizes around 4 nm [see Figure 2(c)].

Photoluminescence measurements were carried out on EBE-grown Si NCs/SiO₂ samples deposited on Si substrates, exciting them with the 532-nm line of a continuous wave Nd:YAG laser. In Figure 4(a), the PL spectra from the samples with $L_{\text{SRO}} = 3.9$ nm and annealed at different temperatures are shown. In the case of the as-deposited sample, no emission is observed, which is in agreement with the fact that the precipitation of the Si excess in the form of nanoaggregates has not taken place yet. In contrast, annealed samples exhibit PL

emission with a broad spectrum in the red-infrared part of the spectrum. The intensity of this PL emission increases with the annealing temperature, achieving its maximum at 1200 °C. A similar evolution has been found for the samples with different L_{SRO} , indicating that the optimum annealing temperature for obtaining improved optical emission matches with the one for having high crystalline quality, as demonstrated from the Raman study.

The PL spectra of the samples with different L_{SRO} and annealed at 1200 °C are shown in Figure 4(b). In this case, the PL intensity decreases as the L_{SRO} increases, exhibiting also a broader lineshape. Considering that the PL lineshape from Si NCs is constituted by a combination of Gaussian contributions (see for instance Refs. 19 and 25), our spectra could be deconvolved using only two Gaussian functions in the energy domain, one of them centered at higher energies (around 750 nm) and another centered at lower energies (around 900 nm). The deconvolution of the PL spectra for samples with $L_{\text{SRO}} = 3.5$ nm and $L_{\text{SRO}} = 4.7$ nm is displayed in Figure 4 (c), exhibiting excellent accordance between the experimental spectra and the Gaussian fits. In Figure 4(d), the band gap energy corresponding to each contribution as a function of L_{SRO} is plotted for all samples annealed at $T_a = 1200$ °C. The peak energy of both contributions decreases for larger L_{SRO} values, which is consistent with the reduction of quantum confinement of carriers in larger Si NCs. However, this trend is more accentuated in the case of the lower-energy contribution (green circles). In addition, the deconvolved peak at lower energies displays an overall intensity which is almost independent on L_{SRO} , in contrast to the intensity of the higher-energy contribution (blue squares), exhibiting a pronounced intensity quenching at larger L_{SRO} [see Figure 4(e)]. Considering the peak energy values and the intensity behavior reported in the literature for Si NCs with similar sizes,^[1–3,25] our observations suggest that the low-energy contribution is directly related to Si NCs emission via radiative electron-hole recombination, whereas the high energy contribution could be

associated to highly-localized defect levels at the Si-SiO₂ interface, in good agreement with Ref. 25.

In order to obtain more information about the origin of both contributions, PL dynamics was studied by exciting the samples with a Nd³⁺:YAG 5-ns-pulsed laser. To perform time-resolved PL spectroscopy, the monochromator was set at two different wavelengths, 850 nm and 650 nm, which have been selected to separately maximize each PL contribution. The PL time decay of the samples annealed at 1200 °C for different L_{SRO} , at 850 nm and 650 nm, is shown in Figure 5(a) and 5(b), respectively. At both wavelengths, the behavior of the PL dynamics suggests two different time evolutions, which could be fitted by the combination of two stretched exponential decay functions, following the typical analysis for Si NCs:^[26]

$$I_{\text{PL}} = A_1 \exp \left[- \left(\frac{t}{\tau_1} \right)^{\beta_1} \right] + A_2 \exp \left[- \left(\frac{t}{\tau_2} \right)^{\beta_2} \right] \quad (1)$$

The first term in Equation 1 represents the PL decay with a faster dynamics, characterized by its decay time τ_1 , stretching parameter β_1 and amplitude A_1 ; the second term describes the slower PL decay, with its own decay time τ_2 , amplitude A_2 , and stretching parameter β_2 . In all cases, the faster contribution exhibits a stretching parameter $\beta_1 = 1$ (i.e., equivalent to a single exponential) and a decay time of $\tau_1 = (140 \pm 10)$ ns, which matches with time response limitations of our experimental set-up. Hence, there are luminescent centers with decay time faster than this value (and thus not measurable by our equipment), which are typically attributed to emission related to SiO₂ matrix defects (probably due to oxygen vacancies).^[27–29]

The slow decay time τ_2 exhibits a different behavior depending on the observation wavelength. Comparing Figure 5(a) and 5(b), one can observe that the low-energy contribution at 850 nm presents decay times τ_2 lower than the high-energy one at 650 nm, which suggests a different nature of the luminescent centers. In addition, the time evolution of PL at 850 nm shows a lower stretching parameter than the curves at 650 nm. In order to study

these parameters in detail, the evolution of τ_2 and β as a function of L_{SRO} are represented for both contributions [Figures 5(c) and 5(d)]. The Figure 5(c) shows that the contribution at 850 nm shows an increase of τ_2 for larger L_{SRO} , obtaining a constant value at L_{SRO} larger than 4.3 nm, whereas the β value slowly increases with L_{SRO} . Analyzing both parameters (τ_2 and β) for the high-energy contribution [see Figure 5(d)], one can see that τ_2 exhibits values around one order of magnitude lower than the low-energy contribution, as well as decreasing at thicker L_{SRO} . Again, the stretching parameter β exhibits the same evolution as a function of L_{SRO} than in the low-energy contribution, in which a clear increase of its value is observed, despite still keeping lower values.

The results concerning the excitonic recombination dynamics can be further discussed in terms of their time evolution. In particular, the stretched exponential behavior exhibited by both low- (850 nm) and high-energy (650 nm) contributions [see Figure 5(a) and Figure 5(b), respectively] already gives relevant information about the emission centers that yield the observed luminescence. The stretched exponential function has typically been ascribed to (i) a dispersion in excitonic recombination times originated by a broad NC size distribution, each NC size population exhibiting different characteristic decay times,^[30,31] (ii) the interaction between neighboring NCs that induce effects related to electron-phonon coupling,^[32,33] or (iii) the degree of dispersion from the electron and hole motion due to disorder within the material.^[34,35] In these three different but correlated frames, the stretching parameter β can be interpreted as a dispersion from the ideal case ($\beta = 1$) of size mono-population of non-interacting (i.e., separated enough) Si NCs. These characteristics allow explaining the observed PL results so far. Indeed, and as can be seen in Figure 5(c) and Figure 5(d), the high-energy contribution presents remarkably lower β values than the low-energy one. This occurrence could be attributed to highly localized defect levels at the Si-SiO₂ interface, with a larger degree of disorder than in the case of the high-energy contribution, in agreement with

the core-shell model. This assumption is supported by the shorter recombination times (τ_2), by about one order of magnitude, which might indicate exciton instability because of insufficient carrier confinement due to high disorder. Finally, Figure 5(c) and Figure 5(d) show how τ_2 clearly increases for the low-energy contribution at thicker SRO layers until saturating at the thickest $L_{\text{SRO}} = 4.7$ nm, since even thicker barriers will not propitiate the precipitation and crystallization of larger NCs, but instead the broadening of the NC size distribution centered around a saturated NC mean size.^[36] In the case of the high-energy component of PL, we observed the opposite trend compared to the low-energy one, with a reduction of the radiative time τ_2 at larger NCs, in agreement with previous reports in similar samples, which indicates luminescence from the amorphous phase at large NCs.

3. Conclusions

To summarize, the results obtained from the different structural and optical techniques employed in this study revealed the presence of two different optically active luminescent centers within our EBE-fabricated samples: size-dependent excitonic recombination typically reported for Si quantum dots (low-energy PL contribution) and highly-localized disorder-based emission (high-energy PL component) tightly related to the NC amorphous shell and/or NC/SiO₂ matrix interface defects. Therefore, by means of the EBE deposition of alternated SiO₂ and oxidized Si (i.e., the SRO) nanolayers and after a proper high-temperature annealing treatment, we have shown that we are able to tune the luminescence yielded by Si NCs. This has been achieved by controlling the deposited SRO thickness and annealing conditions, which results in the modulation of the two PL emission components. Consequently, the adequacy of the EBE technique to prepare high-quality and light-emitting Si nanostructures has been proved, which paves the way for easy-manufacturing Si NC-based optoelectronic devices.

4. Experimental section

Multilayers of SRO/SiO₂ were deposited onto either *p*-type (100)-Si or fused silica substrates by means of electron-beam evaporation. The employed system was a PFEIFFER VACUUM Classic 500 with a Ferrotec GENIUS electron-beam controller equipped with a Ferrotec CARRERA high-voltage power supply. Before the deposition, the substrates were successively cleaned with acetone, isopropyl alcohol, ethanol and deionized water, being agitated ultrasonically in each process. The MLs were grown depositing alternatively SiO₂ and SRO layers, by respectively evaporating SiO₂ and Si targets, both at a rate of 0.5 Å/s. The base pressure in the chamber was 2×10^{-6} mbar and the substrate was kept at 100 °C. An O₂ line (1.5 sccm), equivalent to 6×10^{-5} mbar, was introduced in the chamber during the whole process, avoiding a possible substoichiometry of the SiO₂ and promoting a partial oxidation of the Si (SRO). In order to control the deposition of SRO and SiO₂ layers, nominal and final thicknesses were compared by fabricating a test sample, which consists of two multilayer stacks separated by 10-nm-thick SiO₂ as a reference layer. The first stack (close to the substrate) presents a variation of the SRO layers keeping constant the SiO₂ barriers thickness at 2.0 nm, whereas for the other one the SiO₂ barrier thickness was varied while keeping constant the SRO layers thickness at 2.0 nm. For the study of the optical properties of EBE-prepared Si NCs, different samples were deposited with SRO nominal layers ranging from 1.0 nm to 2.5 nm with a constant SiO₂ barrier with a nominal thickness of 1.5 nm. This multilayered structure was repeated 5 times, adding a 10-nm of SiO₂ as buffer and capping layers. All ML samples underwent an annealing process inside a tubular furnace for 1 h in N₂ atmosphere, at different annealing temperatures ranging from 1000 °C to 1200 °C.

In order to determine the stoichiometry of the SRO and SiO₂ layers, an XPS analysis was carried out using a PHI 5500 Multitechnique System. Bulk samples of both materials, SRO and SiO₂, were required due to the impossibility of the system to distinguish each individual layer in a multilayered structure with nanometer-thick layers. XPS measurements were carried

out in 200-nm thick samples (either SRO or SiO₂) at a depth of about 50 nm, in order to ensure that information only from the bulk of the samples is acquired, with negligible contribution from their surfaces. The structural characterization was carried out by means of TEM. A conventional mechanical polishing method was employed in cross-section geometry with a subsequent low angle Ar⁺ ion milling up to the electron transparency of the sample. TEM images were acquired by a JEOL 2010F microscope, operated at 200 kV and equipped with a field emission gun coupled to a Gatan imaging filter with 0.8 eV energy resolution. EFTEM in scanning mode and HRTEM were employed to analyze the ML structure and the Si NC formation, respectively. The crystallinity of the Si NCs deposited onto fused silica substrate was analyzed by Raman measurements in backscattering configuration with a Horiba Jobin-Yvon LabRam spectrometer, exciting the samples with the 532-nm line of a Nd:YAG laser at room temperature, keeping the power density on the sample at $\sim 5 \times 10^4$ W/cm². The optical properties were determined measuring the photoluminescence emission of the films grown onto Si substrate in a range between 550 nm and 1050 nm, exciting the samples with the 325-nm line of a He-Cd laser, using a power density of 8×10^3 W/cm², and collecting the emitted light with the same experimental setup; the PL intensity of all spectra was corrected by the spectral response of the system. Finally, time-resolved PL measurements were carried out by exciting the samples with the third harmonic line (355 nm) of a BRILLIANT Nd³⁺:YAG 5-ns-pulsed laser at a peak power density of 10^8 W/cm², while inspecting their emission at 650 nm and 850 nm, in order to understand the origin of the different luminescence contributions.

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Figure 1. XPS analysis corresponding to bulk deposition of both SiO_2 and SRO, after annealing at $1200\text{ }^\circ\text{C}$, employed for the fabrication of the multilayered structure. (a) and (b) present the $\text{Si}2p$ signal of SiO_2 and SRO, respectively, deconvoluted by means of pseudo-Voigt fits related to the different oxidation states of Si. (c) and (d) show the spectra of the $\text{O}1s$ for both layers, SiO_2 and SRO, respectively. In this case, (c) displays a single pseudo-Voigt fit ($-\text{O}-$), whereas (d) is deconvoluted into two pseudo-Voigt contributions related to ($-\text{O}-$) and ($-\text{O}-\text{O}-$) oxygen configurations.

Figure 2. (a) EFTEM image obtained after filtering around the Si plasmon peak (~ 17 eV) with a 3 eV energy window. Bright regions in the image correspond to Si-rich oxide (SRO) regions. (b) Relation between nominal and real deposition thicknesses of SiO₂ and SRO layers. (c) HRTEM image in the center of the first stack. Si lattice planes can be observed (highlighted by red lines) for some crystalline nanoaggregates.

Figure 3. (a) Raman spectra corresponding to the samples with 4.7-nm-thick SRO layers for both the as-deposited samples and the ones annealed at different T_a . (b) Raman spectra corresponding to the samples with different SRO thicknesses annealed at $T_a = 1200 \text{ °C}$. In both figures, the pink dotted vertical line indicates the peak position of the bulk crystalline Si signal. In addition, the Raman spectrum of the SiO₂ substrate (grey lines) is added for comparison.

Figure 4. PL spectra corresponding to the samples with (a) constant $L_{\text{SRO}} = 3.9$ nm and annealed at different temperatures, and (b) different L_{SRO} and annealed at 1200 °C. (c) Example of the two-contribution spectra deconvolution carried out on the samples with $L_{\text{SRO}} = 3.5$ (thinnest sample) and $L_{\text{SRO}} = 4.7$ nm (thickest one), both annealed at 1200 °C. (d) Peak energy corresponding to each PL contribution from the samples annealed at 1200 °C, as a function of L_{SRO} .

Figure 5. Time evolution of the PL intensity corresponding to the samples containing different L_{SRO} and annealed at 1200 °C, measured at (a) 850 nm and (b) 650 nm. The corresponding fits to the fast and slow components are also displayed. (c) and (d) plot the slow decay time, τ_2 , and stretching parameter, β , corresponding to the same samples in (a) and (b).

Table 1. Peak positions corresponding to the different contributions of Si2p and O1s, obtained fitting the XPS spectra acquired from SiO₂ and SRO layers.

	SiO ₂		SRO	
	Si2p	O1s	Si2p	O1s
Peak position (eV)	-		98.6	
	100.1	532.0	100.0	532.1
	101.4	-	101.3	533.6
	102.6		102.5	
	103.7		103.7	
Integrated area (arb. units)	7.25	34.90	4.92	17.54
Atomic concentration (%)	34	66	42	58