Characterization of epitaxial and oxidation-induced stacking faults in silicon: The influence of transition-metal contamination

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Photoluminescence (PL) spectroscopy, transmission electron microscopy (TEM), and defect etching have been used to characterize epitaxial stacking faults (ESF) in silicon epilayers grown by low-pressure chemical vapor deposition (LPCVD) and oxidation-induced stacking faults (OISF) in high-purity float-zone (FZ) Si. No dislocation-related luminescence was observed from either ESFs or OISFs grown under clean conditions. Deliberate surface contamination, followed by annealing with Cu, Fe, Ni, Ag, or Au in the range 4×10^{12}–2×10^{16} atoms cm^{-2} introduced dislocation luminescence features, with a maximum intensity at $\approx 4 \times 10^{12}$ atoms cm^{-2}. TEM examination revealed that there was no evidence for precipitation at low levels of contamination but as the contamination level increased metal-related precipitates were observed on the bounding partial dislocations.

The origin of dislocation-related photoluminescence features (D bands) in silicon has been the subject of many detailed investigations.[1] These studies tended to concentrate on correlating the different luminescence features with specific defect types and then trying to understand the electronic transitions involved. Similar studies have been carried out on Si/Ge alloys[2] and bulk Ge.[3] The origin of the luminescence features has not been resolved; it is not clear whether they are due to recombination at reconstructed sites at the dislocation cores or are associated with impurities either trapped in the strain field of the dislocations or interacting at the core.

The role of impurities must be considered carefully, especially the transition metals. These metals are fast diffusers and are known to form deep levels which can readily effect the electrical and optical properties of bulk silicon. These metals are easily accidently incorporated during sample preparation or can be already present in the bulk. This makes it difficult to generate defects under clean conditions, unless extreme care is used during sample preparation in conjunction with sensitive analytical techniques to check the cleanliness. Also the purity of the starting material must be known to ensure that the bulk impurity levels are as low as possible. In order to investigate the effects of the transition metals it is important to be able to control their deliberate introduction both at low and high concentrations, since the concentration will affect the spatial location of the metal impurities around the dislocations either atomically dispersed or as precipitates.

It has recently been demonstrated[4] that dislocations in material free from transition-metal contamination ($< 10^{11}$ cm^{-3}) give no observable D-band luminescence and no

contrast in electron-beam-induced current (EBIC) measurements, while after deliberate Cu contamination ($\approx 10^{13}$ cm^{-3}) both appear strongly. In this letter, we report further investigations of the influence of transition-metal contamination on the origin of the D bands. Epitaxial stacking faults (ESF) and oxidation-induced stacking faults (OISF) were intentionally contaminated with a range of transition metals (Cu, Ni, Fe, Ag, or Au). The effect of the level of contamination in terms of surface concentration (4×10^{11}–2×10^{16} atoms cm^{-2}) has also been investigated for Cu and Ni.

A wide range of epitaxial layers ($T = 850$–$1150\,°C$, $P = 40$–760 Torr, and thickness ≈ 1–$15\,\mu m$) was grown by low-pressure chemical vapor deposition (LPCVD) using a commercial AMC7811 Applied Materials reactor at Plessey Research Caswell. For comparison, epitaxial wafers from two different commercial manufacturers were also investigated. In addition, high-purity float-zone (FZ) silicon wafers were given a special surface treatment and then oxidized under clean conditions to produce OISFs.

For the photoluminescence (PL) measurements, the samples were immersed in liquid helium at 4.2 K and the luminescence was excited using an Ar$^+$ laser tuned to either 457.9 or 514.5 nm. The luminescence was analyzed using a Nicolet 60SX Fourier-transform infrared spectrometer fitted with a Ge diode detector (North Coast). Preferential defect etching and optical microscopy were used to determine the nature of the defects and their densities. The defects were also analyzed in more detail using transmission electron microscopy (TEM). Atomic absorption (AA) spectroscopy was used to determine the transition-metal impurity levels in the epitaxial layers. The epitaxial layers were selectively removed using ultrapure chemical etching solutions and the analyzed using a Perkin Elmer PE3030 AA spectrometer. Similar experiments were

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carried out on whole wafers to determine suitable starting material for producing OISFs. The detection limit for transition-metal impurities in the epitaxial layers was $\approx 2 \times 10^{13}$ atoms cm^{-3}, and $\approx 10^{11}$ atoms cm^{-3} in the bulk. AA analysis was carried out on at least five wafers of each sample type to detect any random variations in the transition-metal contamination and hence enable meaningful comparisons to be made.

The controlled introduction of the transition-metal contaminants onto the sample surface was carried out by backplating from an appropriate transition-metal salt solution. The concentration of the metal ion in solution was measured by AA and the surface contamination level was checked using total x-ray reflection fluorescence (TXRF). Additional TXRF measurements were carried out to determine the uniformity and reproducibility of the plating process and checks were also made from cross contamination (detection limit $< 10^{11}$ atoms cm^{-2}). The samples were RCA cleaned prior to contamination and then annealed in RCA-cleaned quartz furnace tubes in flowing nitrogen gas immediately after contamination. Adjacent sections were RCA cleaned without deliberate contamination and then annealed. Control experiments were also carried out using blank plating solutions. The same plating method was also used to contaminate ultrapure FZ material to make control samples so that the specific luminescence features associated with the transition-metal-related point defects could be observed[5] and hence verify the identity of the contaminant.

There was no D-band luminescence observed from either the OISFs samples or from SFs in epilayers grown at low temperature ($T = 850$ °C) and low pressures (< 120 Torr), only the edge luminescence associated with donor-bound excitons. However, at both higher temperatures (> 850 °C) and higher growth pressures (> 120 Torr), weak D-band luminescence was also observed. All the commercially grown epilayers that contained ESFs showed much stronger D-band (D1 and D2 only) features. The metal content of all these layers was determined using AA. On inspection of the AA analysis it was clear, when comparing layers of both similar thickness and ESF density, that D-band luminescence was only observed when there was a relatively high level of transition metal present ($> 2 \times 10^{13}$ atoms cm^{-3}). The total metal content of the commercially grown epilayers was usually at least 2–3 orders of magnitude higher than that grown in-house at Plessey. TEM examination revealed no unusual features associated with the structure of the ESFs. Also, no evidence was found for metal precipitation.

A selection of epilayer samples that contained a range of ESF densities (10^4–10^7 cm^{-2}) and showed no D bands was deliberately contaminated and then annealed. Following deliberate contamination with either Cu, Fe, Ni, and Ag ($\approx 4 \times 10^{12}$ atoms cm^{-2}) the D bands (D1 and D2 only) could be clearly observed. Figure 1(a) shows the PL spectrum of an as-received epilayer sample containing 10^7 ESFs. Following RCA cleaning, then annealing at 900 °C, there was no change. However, after Cu contamination ($\approx 4 \times 10^{12}$ cm^{-2}) and annealing, the D bands can be
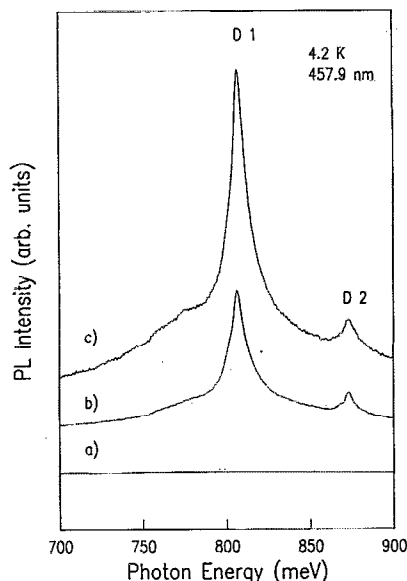

FIG. 1. Photoluminescence spectra of an epilayer sample containing $\approx 10^7$ cm^{-2} ESFs (a) before contamination, (b) after deliberate Cu contamination ($\approx 4 \times 10^{12}$ atoms cm^{-2}) and annealing at 900 °C for 1 h, and (c) after Cu contamination ($\approx 4 \times 10^{12}$ atoms cm^{-2}) and annealing at 900 °C for 1 h, them quenching to room temperature. The spectra are all normalized against the strength of the bound-exciton features at higher energies.

clearly observed [Fig. 1(b)]. Similar results were observed for the OISFs, that is, the OISFs became luminescent after intentional contamination. In addition, deliberate contamination of the epilayer samples that already contained weak D-band luminescence produced a dramatic increase in the D-band luminescence intensity. The positions of the D-band features were approximately constant for the different metals. These results are consistent with other recently published work on dislocations[4] in showing that transition-metal contamination plays an important part in determining the luminescence properties.

Previous work on characterizing dislocations[6] demonstrated that, after contamination, the annealing temperature and the rate at which the sample cools down to room temperature can produce dramatic changes in the PL spectra. The effect of the cooling rate was investigated further: samples containing either ESFs or OISFs were contaminated, annealed, and then quenched to room temperature by immersion in silicone oil. This treatment produced much stronger D-band features. Figure 1(c) shows the PL spectrum from an epilayer sample containing 10^7 ESFs after Cu contamination, annealing, and quenching to room temperature.

The same effects were found for all the metals except for Au. Following Au contamination only one peak was observed at 837 meV and no D bands. The PL spectrum after Au contamination and quenching is shown in Fig. 2(a). This peak was reported previously[6] following contamination of dislocations (generated by plastic deformation) with Cu, Fe, Ni, Ag, and Au, but it is usually much weaker than the D bands. This band is therefore not unique to Au contamination, buy is associated with metal contam-
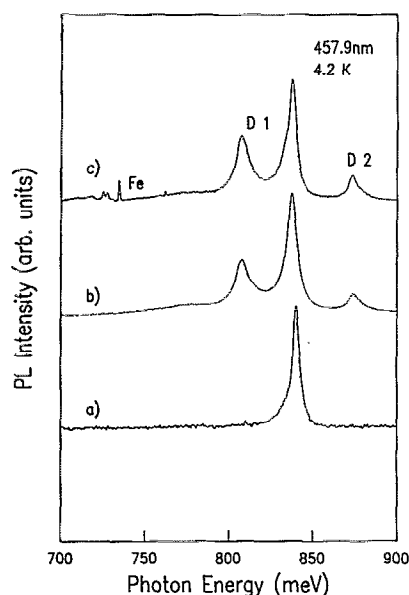
FIG. 2. Photoluminescence spectra of an epilayer sample containing 5×10^7 ESFs after Au contamination, annealing at 900 °C , then quenching to room temperature; (b) sample received the same treatment as (a) then Cu contamination $\approx 4 \times 10^{12}$ atoms cm^{-2} annealing, and quenching; (c) sample received the same treatment as (a) then Fe contamination $\approx 4 \times 10^{12}$ atoms cm^{-2}, annealing, and quenching.

ination of dislocations. Further contamination of the Au-contaminated samples with Cu or Fe and then annealing [see Figs. 2(b) and 2(c)] produced the $D1$ and $D2$ features. The origin of the 837-meV band is not known but further investigations are in progress. These last results demonstrate the complexity of understanding dislocation related luminescence and the effects of transition-metal contamination.

For both types of stacking fault it was found that as the level of contamination (Cu or Ni) was further increased ($> 4 \times 10^{12}$ cm^{-2}) the D-band features decreased in intensity until eventually they could no longer be observed. Figure 3 shows the variation of the intensity of the $D1$ and $D2$ bands as a function of Cu contamination (measured by TXRF) for an epilayer sample containing 5×10^7 ESFs. The D-band peak intensities were normalized to the phos-
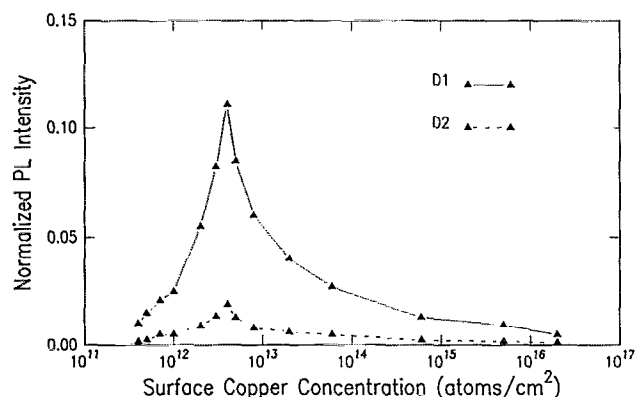
phorus bound-exciton peak arising from the intentional doping of the epilayer. After the D-band intensity decreased the donor-bound-exciton luminescence from the epilayer could still be observed. These results show that the level of contamination is also an important parameter in considering the mechanisms involved in dislocation-related luminescence.

Subsequent TEM analysis has revealed that there are two different regimes of decoration around the stacking faults. At low levels ($< 10^{15}$ atoms cm^{-2}) of contamination there is no evidence of precipitation found on the stacking faults. As the level of contamination is increased further, metal-related precipitates can be observed on the bounding partials in TEM.

EBIC investigation have been carried out on these epitaxial layers and the bulk FZ samples containing OISFs, before and after contamination.[7] It was found that EBIC contrast was observed from all the defects following contamination, whether contaminated on the atomic scale or by precipitates, whereas the dislocation related luminescence features decreased in intensity at high contamination levels until they can no longer be observed. However, at this stage of contamination donor-bound-exciton luminescence can still be observed from the epilayer and not all the luminescence has been quenched. We suggest that as the level of contamination is increased and microprecipitates are formed on the partial dislocations they absorb the centers responsible for dislocation-related radiative recombination.

This investigation has shown that transition-metal contamination plays an important role in the production of D-band luminescence from silicon samples containing either ESFs or OISFs. Further experiments are underway combining EBIC with cathodoluminescence imaging to investigate the relationship between specific defect types, the metal contaminant, and the luminescence.

FIG. 3. D-band intensity ($D1$ and $D2$) as a function of surface Cu contamination (measured by TXRF) for an epilayer sample containing 5×10^7 ESFs.

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