Device grade microcrystalline silicon owing to reduced oxygen contamination

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As-deposited undoped microcrystalline silicon (μc-Si:H) has in general a pronounced n-type behavior. Such a material is therefore often not appropriate for use in devices, such as p-i-n diodes, as an active, absorbing i layer or as channel material for thin-film transistors. In recent work, on p-i-n solar cells, this disturbing n-type character had been successfully compensated by the ''microdoping'' technique. In the present letter, it is shown that this n-type behavior is mainly linked to oxygen impurities; therefore, one can replace the technologically delicate microdoping technique by a purification method, that is much easier to handle. This results in a reduction of oxygen impurities by two orders of magnitude; it has, furthermore a pronounced impact on the electrical properties of μc-Si:H films and on device performance, as well. Additionally, these results prove that the unwanted donor-like states within μc-Si:H are mainly due to extrinsic impurities and not to structural native defects.

Microcrystalline silicon (μc-Si:H) consists of small crystallites (40–1000 Å) which are embedded in an amorphous matrix. A common deposition technique for this material is plasma-enhanced–chemical vapor deposition (PECVD) using high dilution of silane in hydrogen; this combination allows for deposition at rather low temperatures (150–300 °C). Among the various forms of PECVD, the very high-frequency–glow discharge (VHF-GD) method has been shown to be particularly favorable for the growth of μc-Si:H.[1–4]

A problem often encountered with as-grown μc-Si:H is its pronounced n-type character; this n-type character masked for a long time the excellent photovoltaic properties of this material. Nevertheless, this disturbing n-type character could, in recent work,[5,6] be compensated by ''microdoping''; thereby, ''midgap'' μc-Si:H (Fermi level at midgap) was obtained and successfully implemented in a fully microcrystalline photovoltaic device.[7–9] However, the microdoping technique which consists of adding diborane in the parts per million (ppm) range into the gas phase during deposition, is unfortunately difficult to handle; in fact, it has been observed that the Fermi level position reacted thereby sensitively to the deposition rate, to the outgassing of the reactor and to feedgas purity. Thus, this delicate compensation technique is not of real interest for potential industrial applications. To take full advantage of μc-Si:H, it would be highly desirable to replace the microdoping approach by an alternative technological approach that is easier to handle.

It was suggested that either the rather large content of oxygen impurities (10^{19}–10^{21} atoms/cm^3) or native defects within the layers could be responsible for the unwanted n-type behavior.[10,11] Note that conceptually, by microdoping one can counterbalance both possible effects and that it was therefore sofar not clear which effect is actually dominating.

In the following the authors will show that oxygen contamination is indeed mainly responsible for the n-type behavior and that one can therefore omit microdoping if the oxygen content is sufficiently reduced in the deposited layers. Thereby, to monitor whether the μc-Si:H films are truly midgap, the authors will consider the Arrhenius plot of the dark conductivity of these layers; moreover, they have also incorporated identical layers into a fully μc-Si:H p-i-n diode and measured its photovoltaic performance. Additionally, secondary-ion-mass spectroscopy measurements (SIMS) were done to assess the absolute oxygen content in the films.

All layers and cells in this study were deposited in a single-chamber parallel-plate reactor by the VHF-GD technique. The doped contact layers were the same as those optimized in previous work.[1,2] Gas pressure for all layers was kept at 0.4 mbar, resulting in homogeneous films. The i layers were deposited at a dilution level of 2.5% silane into a total gas flow of 100 sccm of hydrogen and silane, at an effective substrate temperature of 220 °C, at a high-frequency power of 6 W (at the impedance matching box) and an excitation frequency of 110 MHz. Under these conditions film growth rate was 1.55 Å/s. The films were deposited on AF45 glass from Schott and the cells on glass coated with textured SnO_2 (Asahi type U). Back contacts for the cells are made of highly textured ZnO and Ag.[12]

The approach followed for the purifying technique applied here, is to try to control all possible oxygen contamination sources: This implied both achieving a sufficiently low reactor outgassing rate of less than 1.5×10^{-6} mbar ℓ/s as well as using a SAES Getters Mono Torr™ room-temperature metallic-alloy gas purifier (the latter reduces the oxygen contamination down to the sub-ppb range in the feedgas). The combination of these two measures leads to a successful reduction of the oxygen content in a-Si:H as well
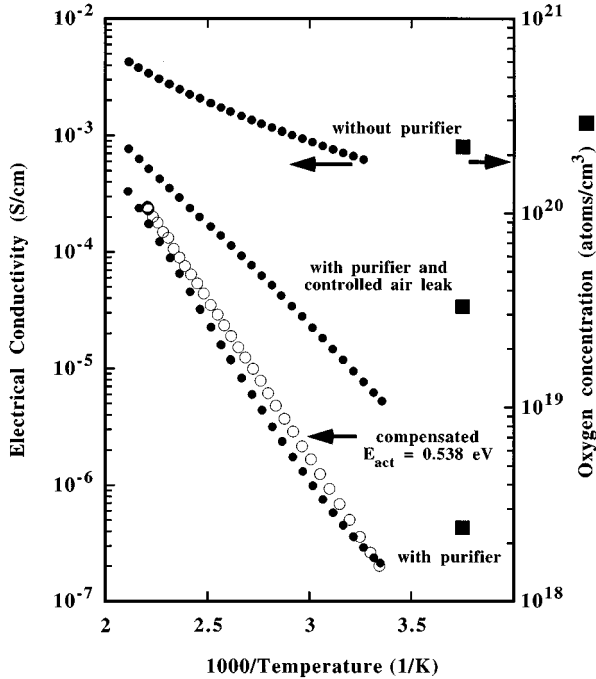
FIG. 1. On the left (dots) Arrhenius plots of the dark conductivity (measured in a coplanar configuration) for three μc-Si:H films deposited by VHF-GD, without microdoping, but with different oxygen purification methods. On the right (squares) corresponding values of oxygen content (measured by SIMS). For purposes of comparison, data pertaining to a compensated ''microdoped'' layer (open circles) deposited in an equivalent reactor under the same deposition conditions, but without a feedgas purifier, is added.

as in μc-Si:H layers.[13,14] Because VHF-GD has the additional advantage of a relatively high deposition rate (as compared with standard GD at 13.56 MHz excitation frequency) this is a further reason for less contaminants to be built in.

Figure 1 shows on the left side the Arrhenius plot of the dark conductivity of three μc-Si:H layers, and on the right side their corresponding values of oxygen content, as measured by SIMS. The layer deposited without the gas purifier shows quite a high room-temperature conductivity in the upper 10^{-4} S/cm and the slope is rather flat. This is an indication that the layer has actually a doped character, due either to an impurity level or, as proposed by earlier work, to native defects.[7,8] The oxygen content of this unpurified layer is about 2.2×10^{20} atoms/cm^3.

A deposition under the same conditions but with the purifying technique described above leads to a successful reduction of the oxygen content down to 2.5×10^{18} atoms/cm^3. Note that other impurities such as carbon and nitrogen vary by only half an order of magnitude. Electrically the effect is drastic as can be seen in the same figure: By reducing the oxygen content by two orders of magnitude dark conductivities at room temperature of low 10^{-7} S/cm are achieved. These low values are similar to those obtained by the compensation technique by means of ''microdoping''. For comparison we have added in the same Fig. 1 the corresponding conductivity measurement for a compensated microdoped layer represented by the open symbols. This layer was deposited in an equivalent reactor under the same deposition conditions. For this compensated microdoped layer an
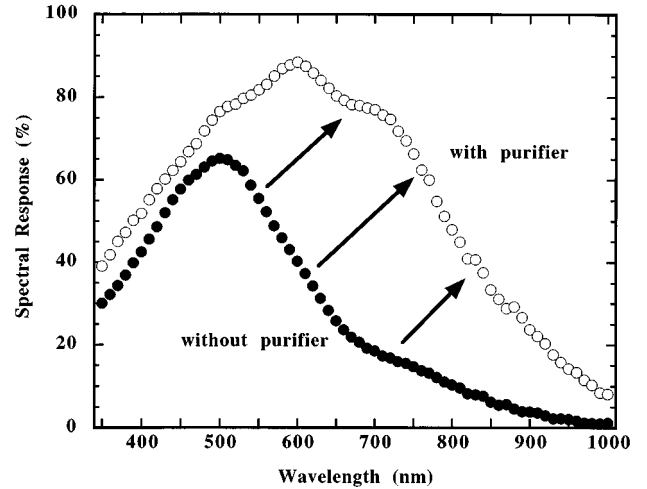
optical gap of 1.02 eV has been evaluated,[15] which is close to the gap of crystalline silicon. Note that the activation energy of this compensated microdoped layer is about half of the optical gap.

To even further demonstrate the effect of the oxygen impurity we deliberately contaminated a μc-Si:H layer during the deposition process. Through a needle valve we simulated an air leak into the reactor. Just before causing the air leak, the outgassing rate was 1.1×10^{-6} mbar ℓ/s and with the controlled hole it rose up to 1×10^{-5} mbar ℓ/s. One sees again that the oxygen content (3.3×10^{19} atoms/cm^3) obtained here corresponds to the dark conductivity measurements. This further experiment suggests that the gas purifier is of no or little help if the outgassing rate of the reactor is not low enough.

Figure 2 shows the spectral response (SR) of entirely μc-Si:H solar cells with the i layers prepared under exactly the same conditions as for the above layer study, both with and without the feedgas purifier. It is well known that the quality of the i layer has a strong influence on the performance and on the SR of a μc-Si:H solar cell device.[8] Again, the effect of reducing the oxygen content by means of using the gas purifier is remarkable and leads to a substantial increase in SR. Reverse biasing while measuring SR shows an excellent saturation of the device deposited with the purifier. In comparison with the compensation technique, now even thicker devices (here up to 2.8 μm thickness) which still allow to separate and collect the photogenerated carriers could be successfully prepared with the purifier technique. This fact may be due both to the reduced impurities as well as to better control of the deposition process. Full characterization under AM 1.5 conditions shows a cell efficiency of 5.3%. Degradation experiments on this μc-Si:H solar cell support our earlier finding that μc-Si:H can be considered as a photovoltaically stable material: Exposure to a high-pressure sodium lamp at about eight suns intensity, for a time period of 264 h and at a temperature of 50 °C did not show any light-induced degradation effect of this cell, as represented in Fig. 3.

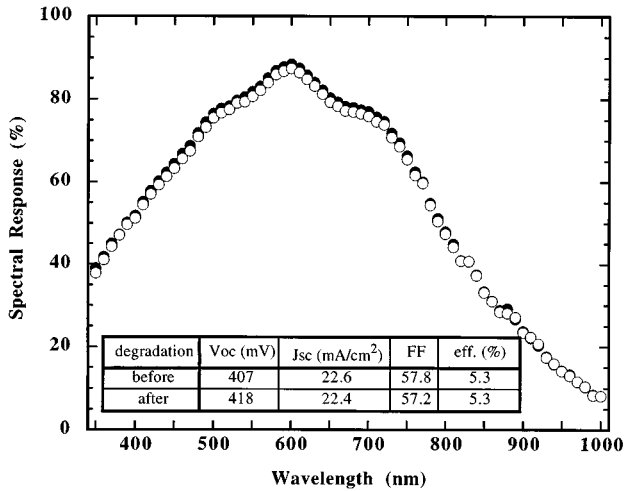FIG. 2. Comparison of the spectral response of two entirely μc-Si:H cells. One produced with and one without a feedgas purifier. The thickness of both cells is 2.8 μm.

degradation	Voc (mV)	Jsc (mA/cm^2)	FF	eff. (%)
before	407	22.6	57.8	5.3
after	418	22.4	57.2	5.3

FIG. 3. Spectral response of a 2.8-μm-thick fully μc-Si:H solar cell produced with the feedgas purifier before and after light soaking (eight suns equivalent high pressure sodium lamp during 264 h at 50 °C).

Thus, the purifier technique results in a substantial enhanced device performance and in even higher solar cell efficiencies than the earlier microdoping approach:[9] meanwhile, a single-junction cell efficiency of 7.7% has been achieved.[16] The microdoping approach could therefore even more than successfully be replaced by the purifying technique.

In conclusion, we have shown that reduction in oxygen impurities acting as unwanted donor state leads to a new photovoltaically active thin-film silicon material, i.e., intrinsic device-grade μc-Si:H, with applications in solar cells, and possibly also, in thin film transistors. The reduction of oxygen contamination could only be achieved by simultaneously controlling the outgassing rate of the reactor and purifying the feedgas. Thereby, increasing the deposition rate

(as was possible with the VHF-GD deposition method used here) also helped to lower the incorporation of impurities.

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