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Resist-free fabricated carbon nanotube field-effect transistors with high-quality atomic-layer-deposited platinum contacts

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Carbon nanotubes are considered as alternative channel material for future transistors, but several challenges exist for reliable fabrication of these devices. In this work, carbon nanotube field-effect transistors (CNTFETs) were fabricated by patterning of Pt contacts using a combination of electron beam induced deposition and area-selective atomic layer deposition (ALD). This bottom-up technique eliminates compatibility issues caused by the use of resist films and lift-off steps. Electrical characterization of a set of 33 CNTFETs reveals that using this direct-write ALD process for Pt patterning yields improved contacts as compared to evaporated Pt, most likely due to improved wettability of the contacts on the carbon nanotube. Moreover, these CNTFETs can be characterized as unipolar *p*-type transistors with a very low off-state current. *Published by AIP Publishing.*
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With Moore's scaling of silicon-based CMOS slowing down,[1] a high mobility material needs to be introduced for the transistor channel to reduce short-channel effects.[2] Carbon nanotube field-effect transistors (CNTFETs) have been explored as an alternative for over a decade, motivated by superior ballistic transport properties and the ultrathin nature of the carbon nanotube.[3–7] Recent progress in growth, purification, and placement of carbon nanotubes demonstrates that the main hurdles for using carbon nanotubes in semiconductor applications are surpassable.[8–12] However, many challenges for reliable fabrication of CNTFETs still remain.

Conventionally, CNTFETs are fabricated by patterning metallic contacts on single-walled carbon nanotubes in a lift-off approach using photo- or electron beam lithography (EBL). There are several issues associated with the use of lithography and lift-off steps for contacting carbon nanotubes. The typical polymer resists used in lithography strongly adhere to the surface of carbon-based materials, which makes it extremely difficult to remove the resist residue afterwards.[13–15] The residue can alter the contact resistance as well as the electrical characteristics of the channel material.[14,16] Furthermore, the adhesion of a metal contact on the inert surface of a carbon nanotube is generally poor.[17] The contact can therefore delaminate during lift-off, and this undesired effect can significantly lower the device yield. Delamination is typically prevented by the deposition of a thin Ti adhesion layer underneath the contacts.[18] However, the work-function of the Ti deviates from what is desired for ohmic contacts,[19] which affects the performance of the CNTFET. Evidently, there are several challenges for reliable nanomanufacturing of CNTFETs.

Previously, we have introduced a *bottom-up* method for the patterning of metallic structures based on atomic layer deposition (ALD).[20–22] This so-called *direct-write ALD* approach combines area-selective ALD[23,24] with the direct-write patterning technique of electron beam induced deposition (EBID)[25,26] as illustrated in Fig. 1. Although EBID has been used to fabricate carbon nanotube-based devices, such as pressure sensors,[27] this technique is not suitable for fabricating high-quality CNTFETs due to the poor material quality that is typically obtained by EBID (purity of only 15 at. % Pt with the remainder being amorphous carbon).[28] In the two-step direct-write ALD method, an ultrathin seed layer is patterned by EBID, followed by area-selective ALD growth on the seed layer pattern. The direct-write character of this technique completely eliminates the need for resist films or lift-off steps. The absence of resist residue may give a lower contact resistance and a higher carrier mobility in the carbon nanotube channel. Moreover, the elimination of the lift-off step improves the device yield by avoiding delamination issues.

In addition to the merits described above, contact metallization by ALD is already interesting in itself, and has not been studied before. The quality of electrical contacts to carbon nanotubes is known to be determined by the work function of the contact material, as well as by the wetting interaction of the material on the carbon nanotube.[19,30] Metals with a high work function, such as Pd (5.1 eV) or Pt (5.7 eV), should form ohmic contacts to carbon nanotubes because the Fermi level of the metal is in the valence band of the carbon nanotube. This has been demonstrated for Pd, resulting in transistors with ballistic charge transport.[31] However, a lower performance has been reported for Pt contacts,[29,32,33] which has been attributed to a poor wetting of the Pt on the carbon

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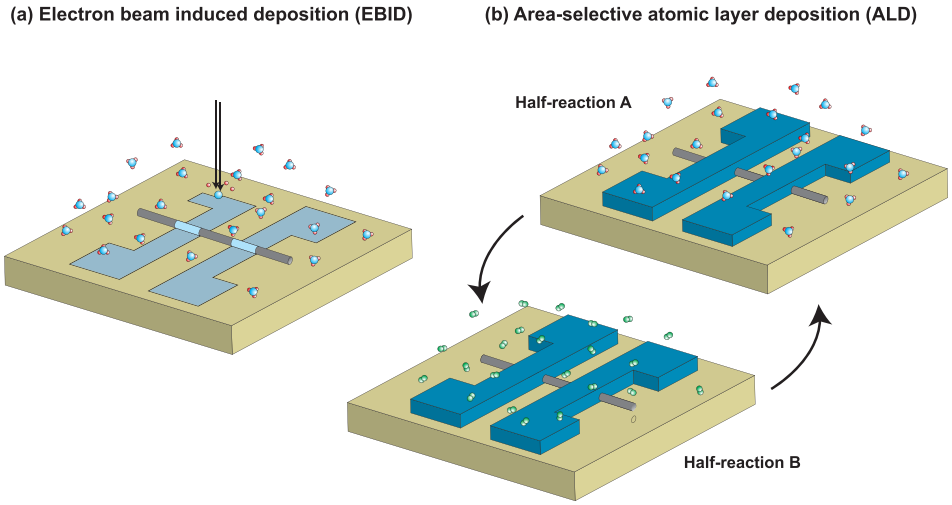

FIG. 1. Schematic representation of the patterning of source and drain contacts on a nanotube by direct-write ALD. A thin seed layer is patterned by electron beam induced deposition (EBID). Subsequently, the pattern is thickened by area-selective atomic layer deposition (ALD).

nanotube.[31,34] Contacts deposited by ALD may result in a better wetting interaction with the carbon nanotube surface due to the chemical nature of the ALD technique.

In this work, CNTFETs were fabricated by using direct-write ALD of Pt for the deposition of contacts to the carbon nanotubes. A set of 33 devices was electrically characterized and compared to CNTFETs prepared with the conventional fabrication scheme. CNTFETs were fabricated in back-gate geometry using *p*-doped Si substrates covered with a 10 nm thermal SiO_2 dielectric. Carbon nanotubes synthesized by laser ablation (1–3 μm long, 0.5–1.5 nm diameter) were purified[35] and dispersed on these substrates. The source and drain contacts were patterned by Pt EBID using an electron dose of 15 pC/μm^2, and thickened by 1000 cycles of Pt thermal ALD. This leads to contacts of ~45 nm thick when assuming a nominal growth rate of 0.045 nm/cycle. In addition, a reference sample was prepared using the conventional fabrication approach, i.e., by electron beam lithography (EBL) in PMMA resist and evaporation of Ti/Pd/Au contacts (0.5 nm Ti, 15 nm Pd, 15 nm Au). The source and drain contacts on both samples were patterned 300 nm in width in order to exclude short contact length effects in the analysis,[36] and were defined with a channel length of 300 nm. The samples were kept in vacuum during the electrical characterization.

Figure 2(a) depicts a top-view scanning electron microscopy (SEM) image of a contact pattern fully prepared by direct-write ALD. The zoomed-in image in Fig. 2(b) shows the Pt lines that form the source and drain contacts of the CNTFET devices. A cross-sectional transmission electron microscopy (TEM) of such a contact is shown in Fig. 2(c). Interestingly, it does only show a dense Pt layer, and no separate layer at the interface with the thermal SiO_2 originating from the EBID seed layer. More specifically, the large grain at the left side of the TEM image extends all the way to the interface with the SiO_2 dielectric, without being interrupted by an additional interface. This confirms that the initial EBID seed layer was extremely thin and may have been purified during ALD, as discussed in detail in previous work.[22] The thickness of the contact is ~35 nm, which is thinner than expected based on the number of ALD cycles, suggesting that the ALD growth initiated after a short nucleation delay.[22]

The CNTFET devices were electrically characterized to evaluate the contact quality (see Fig. S1 in the supplementary material for a SEM image of this sample). Figure 3(a) shows five representative transfer characteristics ($V_{ds} = -0.5$ V) of CNTFETs with Pt direct-write ALD contacts. All the 33 devices perform as *p*-type transistors with I_{on}/I_{off} ratios of 10^4–10^7. The contact quality was evaluated by determining the on-current of these 33 CNTFETs for a gate overdrive of 0.5 V ($V_{gs} = V_{th} - 0.5$ V). Figure 3(b) depicts the on-current distribution, showing the percentage of devices in every decade in on-current. The graph reveals that the on-current distribution of the CNTFETs with Pt direct-write ALD contacts is comparable to the distribution for conventionally fabricated Ti/Pd/Au contacts, which indicates a similar contact quality. About half of the devices have an on-current in the 0.1–1 μA decade, one-third in the 10^{-2}–0.1 μA decade, and 12% in the 1–10 μA decade. The on-current distribution is also very similar to the data presented in a previous study with Pd contacts in a comparable device geometry.[19] Please note that carbon nanotubes with diameters in the range of 0.5–1.5 nm were used (and therefore with different bandgaps), which explains the variation in device performance.

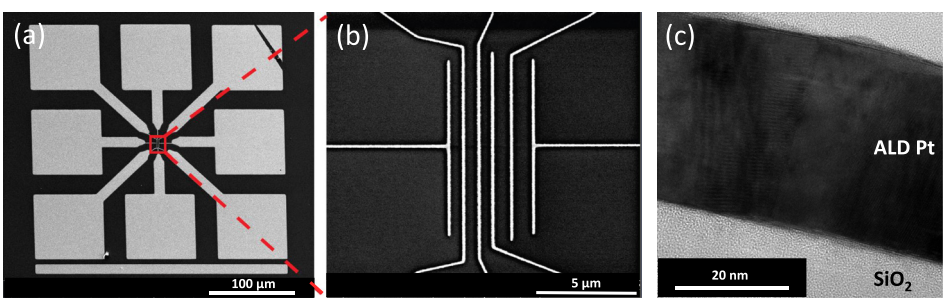

FIG. 2. (a) and (b) Top-view scanning electron microscopy (SEM) images of a contact pattern synthesized by direct-write ALD of Pt. (c) Dark field cross-sectional TEM (HAADF) image of a Pt direct-write ALD contact.

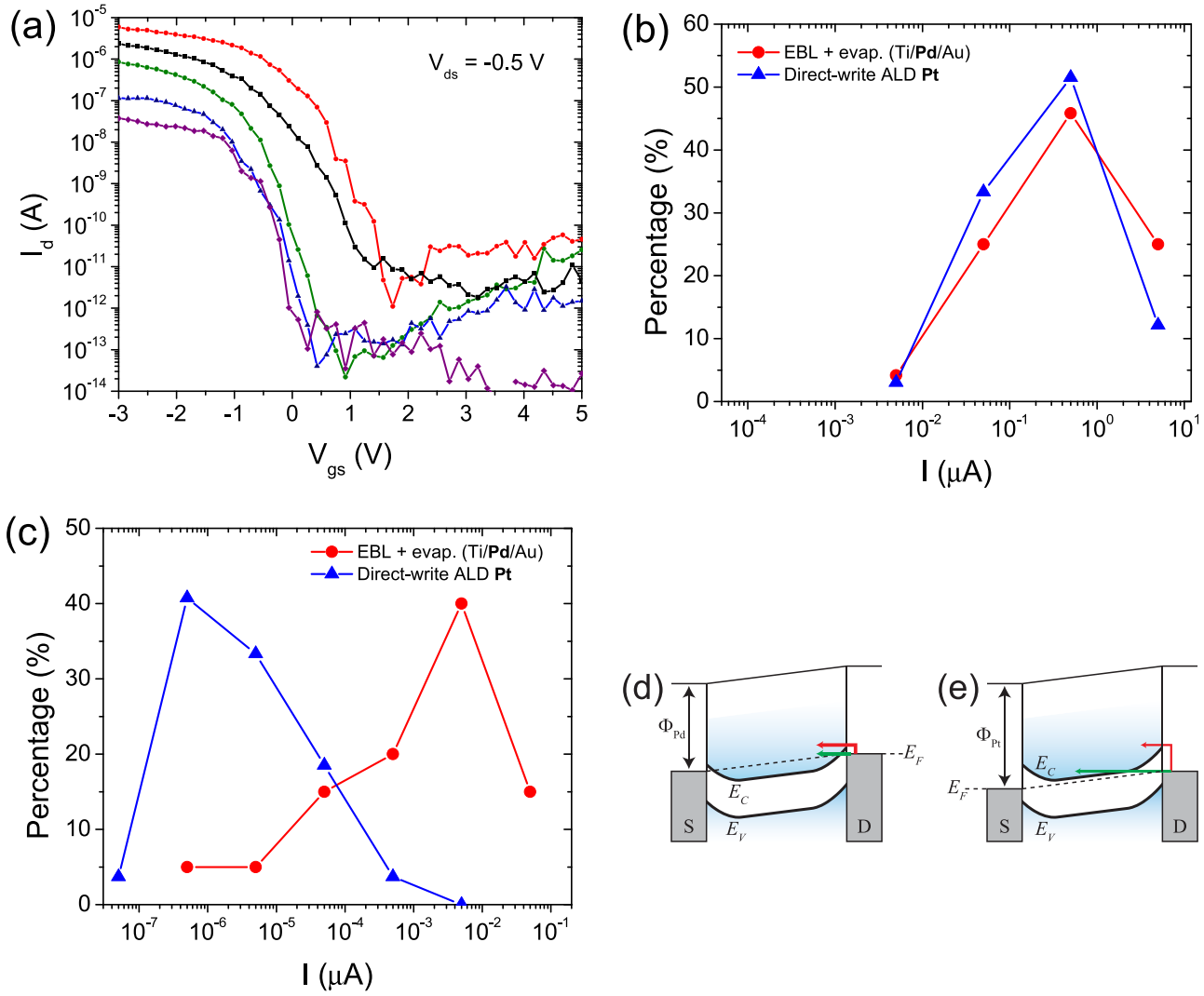

FIG. 3. (a) Five representative transfer characteristics from the set of 33 CNTFETs fabricated using direct-write ALD of Pt. (b) and (c) Comparison between the (b) on-current (at $V_{gs} = V_{th} - 0.5$ V) distributions and (c) *n*-branch current (at $V_{gs} = V_m + 3.0$ V with V_m at the minimum current) distributions, for CNTFETs with Pt direct-write ALD contacts and conventionally fabricated Ti/Pd/Au contacts. (d) and (e) Energy level diagrams for CNTFETs operated at $V_{gs} > 0$ and $V_{ds} < 1$ V with (d) Pd contacts and (e) Pt contacts. The Schottky barrier for electron injection into the conduction band is higher when using Pt as the contact material due to the higher work function of Pt.

The performance uniformity of CNTFET devices is predominantly determined by intrinsic properties of the carbon nanotube (e.g., differences in diameter and defect densities), and much less by variation in the contacts. The direct-write ALD approach is compatible with the strategy of including multiple carbon nanotubes in a device in order to improve the uniformity of device performance.[29]

As mentioned earlier, evaporation of Pt is known to result in contacts of poor quality.[32,33] The unparalleled high contact quality obtained in this study for Pt as the contact material suggests that direct-write ALD provides Pt that has a better wetting interaction with the carbon nanotube as compared to Pt deposited by evaporation. This is surprising when considering that Pt ALD initiation on carbon nanotubes has been reported to be challenging.[37–39] However, EBID of Pt has been achieved on carbon nanotubes in several studies.[27,40] The microstructure of the EBID seed layer consisting of Pt grains embedded in amorphous carbon[41] most likely plays an important role in the nucleation of Pt ALD on the carbon nanotube. The Pt grains catalyze the surface reactions of Pt ALD growth,[22,42] while the carbon sticks more easily to the surface of the carbon nanotube than Pt thereby facilitating the wetting. Alternatively, it could be that Pt growth only occurs on the SiO_2 surface and that the carbon nanotube is eventually "buried" in the deposited Pt by spill-over of the growth from the SiO_2 surface.[43] If this is the case, ALD is still expected to yield a contact that nicely follows the contours of the carbon nanotube, due to the excellent conformality of the technique. In the same way, ALD of HfO_2 dielectric layers on carbon nanotubes has been reported to lead to CNTFETs with excellent performance,[33] even though the growth of the dielectric relied on the spill-over of the HfO_2 deposited on the SiO_2 substrate.[33,43]

The transfer characteristics of Fig. 3(a) show an off-state behavior that deviates from what is observed for the reference dataset (see Fig. S2 in the supplementary material). The reference CNTFETs with conventionally fabricated Ti/Pd/Au contacts can be described as ambipolar transistors with a significant current in the *n*-branch of the *I*–*V* curve, similar to the data previously reported in the literature.[5,36,44]

Figure 3(a) suggests that CNTFETs with direct-write ALD Pt contacts are better described as unipolar transistors with a lower current for $V_{gs} > 0$. It should be noted that for the application of *p*-type CNTFETs in integrated circuits, it is desirable to suppress the *n*-branch as much as possible to reduce the power dissipation in the off-state. Figure 3(c) shows a comparison of the *n*-branch current (at $V_{gs} = V_m + 3.0\,\text{V}$ with V_m at the minimum current) determined for the two datasets. This graph reveals that the *n*-branch current distribution is shifted three orders of magnitude in current, which clearly illustrates the significantly reduced *n*-branch current for CNTFETs fabricated using the Pt direct-write ALD.

The current in the *n*-branch of the *I*-*V* curve is known to depend on the carbon nanotube diameter, the equivalent oxide thickness (EOT), as well as the work function of the contact material. The same source of carbon nanotubes and the same substrates (with 10 nm SiO_2 dielectric) were used for the two datasets, ensuring that the difference is caused by the contacts. This leaves two main differences between the two types of CNTFETs that could be responsible for the differences in off-state behavior: (i) the absence of resist residue or (ii) the contact material employed (Pt vs. Ti/Pd/Au). The unipolar character of the direct-write ALD synthesized CNTFETs could be due to a higher work function of the Pt contact, caused by the use of Pt (5.7 eV instead of 5.1 eV for Pd) and/or the absence of resist residue and Ti at the interface. A higher work function theoretically leads to a higher Schottky barrier for electrons (see Figures 3(d) and 3(e)), which translates into a lower current in the *n*-branch of the transfer characteristic. The precise work functions of the direct-write ALD Pt and the evaporated Ti/Pd/Au contacts will be measured in future experiments.

In principle, a higher work function should also give a lower Schottky barrier for holes, and result in a higher on-current. However, an on-current distribution similar to the Ti/Pd/Au contacts was observed (Fig. 3(b)), which suggests that the wetting interaction of the Pt synthesized by direct-write ALD is not as good as the wetting interaction of the evaporated Ti/Pd/Au, although it is significantly improved as compared to evaporated Pt. In other words, the combined effect of the higher work function of Pt and a moderate wettability gives an on-current distribution for the Pt direct-write ALD contacts that is similar to the conventional Ti/Pd/Au contacts. It is important to note that the direct-write ALD process was only optimized to enable patterning of contacts with targeted dimensions, and not for the deposition of material with a good wetting interaction on the carbon nanotube. Assuming that direct-write ALD results in Pt growth on the carbon nanotube itself, it may be possible to improve the wetting interaction by, for example, using a slightly thicker EBID seed layer. This potentially leads to Pt contacts that outperform the state-of-the-art Pd contacts.

In summary, we studied the fabrication of CNTFETs using a combination of EBID and ALD for the patterning of the source and drain contacts. From electrical characterization of a set of 33 devices, it is deduced that direct-write ALD of Pt yields contacts with a better wetting interaction on the carbon nanotube as compared to Pt deposited by other means. The CNTFETs can be described as unipolar *p*-type transistors with a reduced current in the off-state, which is likely due to the higher work function of Pt. The resist-free patterning of direct-write ALD potentially gives a lower contact resistance and a higher mobility of charge carriers due to the absence of resist residue, which will be studied in more detail in future experiments.

See supplementary material for additional information about the CNTFETs prepared by direct-write ALD, and for transfer characteristics from the reference dataset.

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