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UV ozone treatment for improving contact resistance on graphene

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Optimized UV ozone cleaning of graphene layers on SiO_2/Si substrates is shown to improve contact resistance of e-beam evaporated Ti/Au contacts by three orders of magnitude (3×10^{-6} Ω-cm^2) compared to untreated surfaces (4×10^{-3} Ω-cm^2). Subsequent annealing at 300 °C lowers the minimum value achieved to 7×10^{-7} Ω-cm^2. Ozone exposure beyond an optimum time (6 min in these experiments) led to a sharp increase in sheet resistance of the graphene, producing degraded contact resistance. The UV ozone treatment is a simple and effective method for producing high quality contacts to graphene. *© 2012 American Vacuum Society*. [http://dx.doi.org/10.1116/1.4754566]

I. INTRODUCTION

To fully exploit the advantages of graphene for applications in ultra-fast electronics[1,2] and sensors,[3–5] it is necessary to develop Ohmic contacts with low specific contact resistance. Numerous groups have reported specific contact resistances, ρ_c, around 5×10^{-6} Ω.cm^2 (Refs. 6–12) with a low value of 10^{-7} $\Omega\cdot$cm^2 obtained for Ti/Pt/Au metal stacks on epitaxial graphene.[12] Robinson *et al.*[12] investigated the properties of a number of different contacts to graphene (Al/Au, Ti/Au, Ni/Au, Cu/Au, Pt/Au, and Pd/Au) and found that most metallizations resulted in similar specific contact resistances independent of the work function difference between graphene and the metal overlayer. In any practical processing sequence, the graphene surface will be exposed to different chemicals, such as photoresist residues,[13,14] oxygen atoms,[15] and even adsorption of water molecules, which have been shown to significantly influence the resistivity of the graphene.[16–18] Thus, conventional lithographic processing for graphene devices needs careful attention to avoid degrading the surface properties.[19,20]

Several groups have reported that low power O_2 plasma treatments can improve contact resistances and adhesion for metals on graphene by removing photoresist residues and making the surface hydrophilic.[12,21,22] High contact resistance between graphene and metals is the result of the low interaction energy between the metal and carbon atoms.[20] Chemical reaction with O radicals imparts hydrophilic properties to graphene more effectively than the chemical reaction of H and N radicals or physical bombardment with Ar ions.[22] However, graphene surfaces are susceptible to damage by energetic ions in oxygen plasmas.

In this Letter, we report on the use of UV ozone treatments to improve contact resistance between graphene and metals. There is an optimum ozone exposure time beyond which the sheet resistance of the graphene increases rapidly, degrading the contact resistance of subsequently deposited Ti/Au contacts.

II. EXPERIMENT

The monolayer graphene used for these experiments was grown on 25 μm thick copper foil in a quartz tube furnace system using a chemical vapor deposition method involving methane and hydrogen gases.[5] After PMMA was coated on top of the graphene, the PMMA/graphene/Cu-foil structure was dipped in diluted ammonium persulfate ($H_8N_2O_8S_2$) solution to selectively etch only the Cu-foil. Then, the PMMA/graphene layer was transferred to the SiO_2Si substrate, followed by removal of the PMMA using acetone. While we did not make gated structures in this study to directly get mobility and Dirac point data, in similar layers on SiO_2, we measured mobilities at 300 K of ~3900 cm$^2\cdot$V s. This is competitive with most literature values.

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To study the effects of UV ozone treatment (UVOCS UV Ozone Cleaning System Model 70606B) prior to metal deposition, samples were exposed for 1–8 min at room temperature. Ozone cleaning is effective in removing surface contamination layers in other materials systems.[23] Ti/Au contacts were made to the graphene by evaporation through a stencil mask. The contact pad dimension was 200 × 200 μm^2, large enough that fringing fields do not have an impact on contact resistance measurements. The total device dimension was 1000 × 1000 μm^2. The sheet resistances and contact resistances were measured by the transmission line method. A schematic of the process flow is shown in Fig. 1.

III. RESULTS AND DISCUSSION

Figure 2 shows the contact resistance of the Ti/Au on graphene was 4×10^{-3} Ω-cm^2 without any treatment. Optimal contact resistance values of 3×10^{-6} Ω-cm^2 were achieved when the graphene surface was treated for 6 min to remove surface contamination. Previous reports have shown that high levels of carbon–oxygen single and double bonds exist on processed graphene surfaces from residual photoresist residue.[12] Even atmospheric exposure is likely to leave surface residues that could prevent intimate contact with deposited metals. The improvement of 3 orders of magnitude in contact resistance on ozone treated samples shows the effectiveness of the ozone in providing an optimal surface for making good contacts. Beyond 6 min exposures, the contact resistance significantly degrades—this corresponds to an increase in the sheet resistance of the graphene.

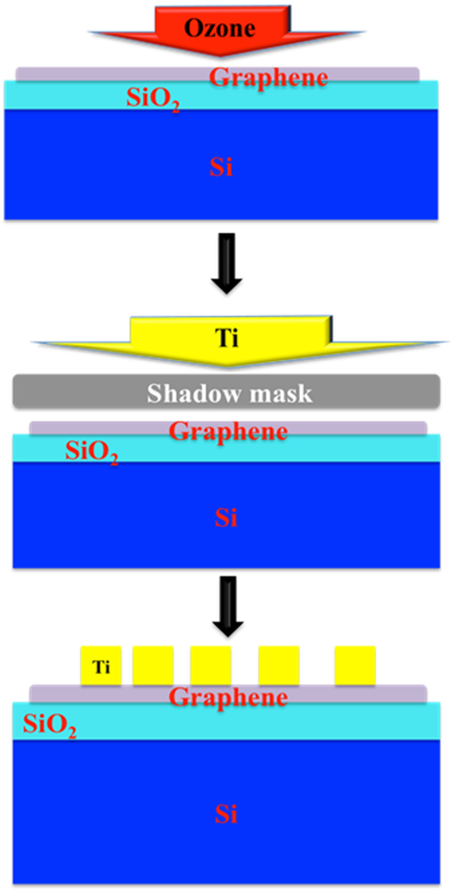

FIG. 1. (Color online) Schematic diagram of the process flow for measuring the effect of ozone treatment on contacts to graphene.

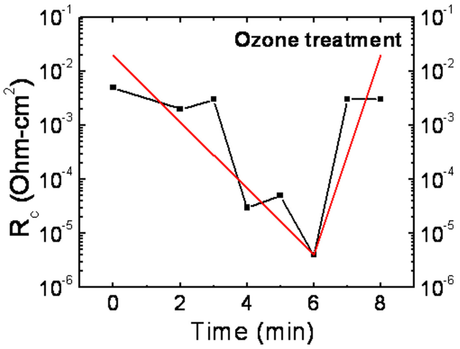

FIG. 2. (Color online) Specific contact resistance as a function of ozone treatment time.

The sheet resistance of graphene was not changed significantly by ozone treatments up to 6 min, as shown in Figs. 3 and 4, showing that graphene was not damaged by ozone treatments for short times. If the ozone exposure time was longer than 6 min, the graphene resistance also increased. We have seen in separate experiments that exposure to the flux of oxygen atoms, molecules, and radicals in a plasma environment increases the resistance by more than 3 orders of magnitude. The strong effect of atomic oxygen is consistent with previous reports[12,15,23–25] but does point out that using an O_2 plasma ashing step to remove photoresist residues is not benign. The UV ozone environment is much more benign but still can degrade the electrical properties of graphene for extended exposures.

After the optimum ozone treatment for 6 min, subsequent thermal annealing of the deposited contacts was found to improve the contact resistance of the Ti/Au. The contact resistance was typically reduced by a factor of ∼4 over most of the examined temperature range, with minimum values of 7×10^{-7} Ω-cm^2 when the metal contacts were annealed at 300 °C for 10 min. The improvement with annealing is

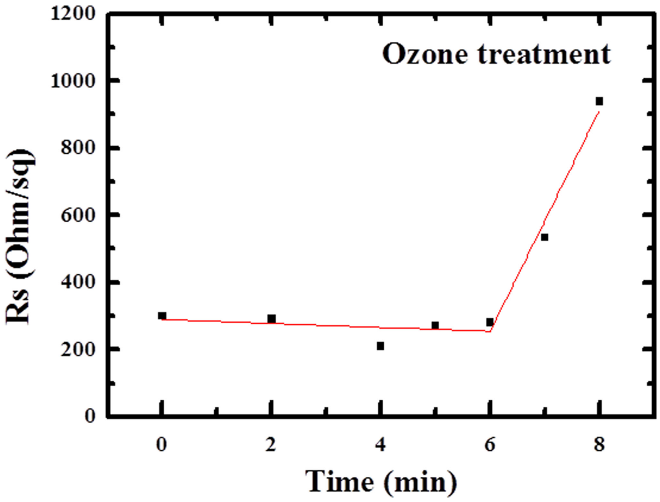

FIG. 3. (Color online) Sheet resistance of graphene as a function of ozone treatment time.

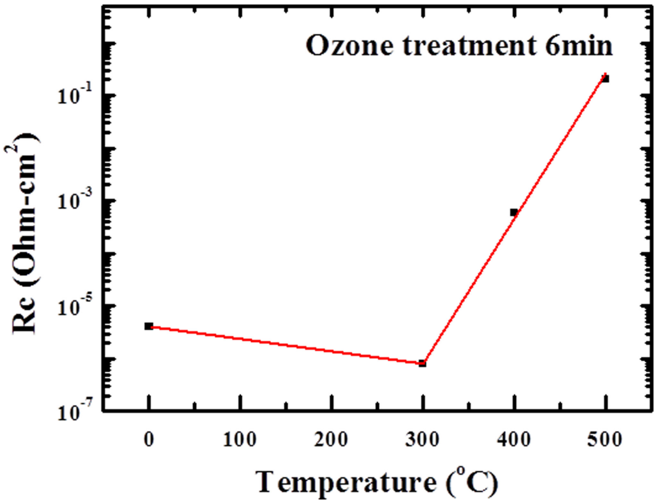

FIG. 4. (Color online) Specific contact resistance as a function of different annealing temperatures for a fixed ozone treatment time of 6 min.

consistent with the results of Robinson *et al.*,[12] who also found that carrier mobility in the graphene was generally improved with annealing.

IV. SUMMARY AND CONCLUSIONS

In conclusion, the combination of UV ozone exposure prior to metal contact deposition and annealing of the contacts produces minimum specific contact resistances values of 7×10^{-7} Ω-cm^2 for Ti/Au on graphene layers on SiO_2/Si substrates. This is an attractive option for cleaning the graphene surface without issues related to energetic ions in O_2 plasma exposures.

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