Nanoscale Processing by Adaptive Laser Pulses

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We theoretically demonstrate that atomically-precise “nanoscale processing” can be reproducibly performed by adaptive laser pulses. We present the new approach on the controlled welding of crossed carbon nanotubes, giving various metastable junctions of interest. Adaptive laser pulses could be also used in preparation of other hybrid nanostructures.

Understanding and fully controlling growth, structural modifications and coalescence of nanoscale materials has a top technological priority. Many excellent examples of such systems can be found among the numerous types of recently discovered nanotubes [1–3]. These unique materials are usually grown under rather poorly understood conditions using plasma [4], laser [5] and other strongly non-equilibrium processes, where catalytic atoms can activate “zipping” of chemical bonds [6].

Although artificial nanoscale materials resemble biomacromolecules, they do not possess “inheritable memories”, analogous to DNA, crucial for their exact repro-duction. Thus our principal question is, if we can develop effective atomically-precise processing methods, that can reproducibly prepare such systems. This goal has been, for example, achieved in a molecular beam growth of superlattices, where nanoscale patterns in one dimension are practically under full control [7].

It would be especially attractive to achieve a precise control over some advanced structural modifications. An example is coalescent “welding” of tubular structures [8], which could lead in crossed nanotubes [9] to preparation of strong light-weight nets. As just demonstrated experimentally [10], atomically-smooth welded nanotube structures can be induced by irradiation with electrons of MeV energies. Unfortunately, control over this process is so far limited, and thermal healing of the radiation-induced defects [11] is only partial.

It thus becomes very interesting to consider thermal welding of nanotubes, driven by an externally applied pressure. Recent simulations [12,13] have revealed that this approach could produce defect-free welded structures, with deep energy minima. On the other hand, practical applications could also largely benefit from a reproducible preparation of various metastable atomically-precise structures, with shallow energy minima. An example are nanotube junctions with a “quasi-continuous” variation of their atomic structures.

Here, we address this challenging task, and explore the possibility of a reproducible welding of nanotubes, by “adaptive” laser pulses. A feedback control of ultrashort chirped pulses is already applied in traditional macro-welding of thin films [14]. A precise nanoscale processing could, in principle, be performed by more sophisticated pulses [15], prepared in optimal control techniques [16], that can selectively break molecular bonds in gases and liquids [17]. Such pulses possess many degrees of freedom in their complex shaping and tuning, with the potential for a storage of “production informations”.

In Fig. 1, we present a scheme of the controlled welding of crossed nanotubes, realized by their local excitation with adaptive laser pulses. These pulses induce interband electron transitions in a micron-size region, where the hot carriers emit LO phonons. The generated phonons locally decay and heat nanotubes below their melting point ($T_{\text{melt}} \approx 4000$ K) [18]. Reconstruction of C bonds is thus induced thermally in the contact area, where nucleation energies of potential defects are decreased by external pressure. Since the flipped bonds are selected and directed by the configuration of the whole system and the applied pressure, light pulses mostly control the total extent of coalescence. The joined region preserve the hexagonal atomic pattern if the tube structures are complementary (armchair/azigzag).

We start the analysis of the welding control with the description of the nanotube excitation by inhomogeneous light intensity $E(x,t)$ [19]. From the Fermi’s Golden rule we can estimate the electron/hole injection rate, $\dot{n}_{e(h)}(x,t) \propto |E(x,t)|^2$, in the conduction/valence band of the crossed SWNT. Typically, we use the field inten-
\[ \dot{\rho}_i = \frac{\rho_{i-1}}{\tau_i} + \frac{\rho_{i+1}}{\tau_i} - \rho_i \left( \frac{1}{\tau_i} + \frac{1}{\tau_i} \right), \]

where the nucleation time \( \tau_i^+ (\tau_i^-) \) gives the transition rate for creation of \( i + 1 \) \((i - 1)\) defects, if the system has \( i \) defects. The nucleation processes are activated by the temperature at the tube crossing, so the times are

\[ (\tau_i^\pm)^{-1} \approx 2 N_{at} \nu_0 \exp \left[ -E_{\pm}^\star (i) / k_b T \right]. \]

Here, \( N_{at} \approx 20 \) is the effective number of C atoms in the local region, \( \nu_0 = 10 \text{ ps}^{-1} \) is the vibrational frequency, used also in \( \mathcal{E}_p \), and \( E_{\pm}^\star (i) \) are activation barriers of the \( i + 1 \)-th and \( i - 1 \)-th defects for structures with \( i \) defects.

We model these barriers as follows,

\[ E_{\pm}^\star (i) = 6 - \Delta \exp\left[ \left| -i - j_0 \right| \pm 0.5 / D_i \right] \text{ eV}, \]

where we assume that the pressure-induced barrier shift, \( \Delta > 0 \), is exponentially relaxed with the growing number \( i \) of defects, since the pressure (motion of the tubes) cannot follow the fast (pulsed) coalescence. In numerical testing, we apply ns welding pulses, separated by \( \mu s \) periods. After the first pulse, the strain \( \varepsilon \) can return to its initial value in all structures, irrespective of their number of created defects \( j_0 \). In the next pulse, structures with different number of defects \( j_0 \) thus effectively start their evolution with the same barriers \( E_{\pm}^\star (i = j_0) = 6 - \Delta \exp[\pm0.5 / D_i] \). Here, the shifts \( \pm0.5 \) reflect the pressure-induced asymmetry in transitions increasing/decreasing the number of defects by one, which is the driving force of the coalescence.

Let us now discuss in more details practical realization of the welding control. In experiments, we can search the optimal field \( E(t) \) in a feedback learning loop (see inset of Fig. 4), where we impose our welding requirements. In contrast to the MBE [7], where growth of individual monolayers is controlled in situ, here the light pulses need
where we fix the parameters \( \sigma \) and configuration (see above), the field practically only controls the flipped bonds are largely selected by the system contributions of \( T \) which reflects the welding requirements [16] and enables theoretical testing of the method. Since our goal is to theoretically adjust to the experimentally obtained structures.

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In order to control the nanotube welding, we can take advantage of the fact that the pressure-induced lowering of the barriers \( E^*_i(i) \) stops during the fast creation of the first \( D_i \) defects. Thus, we use short light pulses, heating the system in such a way, that less than \( D_i \) defects are created by each of them, so that fluctuations in \( \sigma_D \) remain suppressed by the growing barriers \( E^*_i(i) \). If we try to induce more than \( D_i \) defects by a single pulse, then the tubes would have to be largely heated, since the barriers are not lowered any more by pressure. Therefore, structural fluctuations would significantly grow and welding could spread without control in the whole region of the crossed tubes. This means that metastable structures with more than \( D_i \) defects would have to be prepared by several pulses, each generating \( \langle N \rangle < D_i \) defects.

We now test these ideas by solving Eqns. (1-6). Since the flipped bonds are largely selected by the system configuration (see above), the field practically only controls the progress of welding. Therefore, we can search it in a Gaussian form \( E(x, t) = E_0 \exp(-x^2/\sigma_x^2 - (t-t_0)^2/\sigma_t^2) \), where we fix the parameters \( \sigma_t = 2.5 \) ns \((t_0 = 4 \) ns\) and \( \sigma_x = 1 \) \( \mu \)m, and thus choose \( E_0 \) as the only varied parameter. In each iteration, of the learning scheme in Fig. 4, we apply three identical (separated) pulses to the system. Then we calculate the difference \( F \), and let \( E_0 \) to evolve until \( F \) is minimized. In real experiments, we can also vary the shapes of the pulses, in order to fit more complex transient conditions.

Here, we assume that the nanotubes are in a contact with each other at the crossing and with four contacts (two for each), separated \( 3 \) \( \mu \)m away from the tube crossing. They pull the two tubes in opposite directions and thus maintain the vertical force \( F = 5 - 15 \) nN [13] at their crossing. We assume that the force leads to the model parameters \( \Delta \approx 4 \) eV and \( D_i \approx 15 \), used in Eqn. (5). The contacts also provide heat sinks, and are thus held at the temperature \( T_0 = 300 \) K. In this geometrical configuration, the nanotubes move and restore the force on \( \mu \)s timescale, after each welding pulse.

Figure 2 shows the temperatures \( T(x = 0, t) \) at the crossing, induced by excitation with any of the three (separated) laser pulses. By requesting that the pulses create in total \( \langle N \rangle \approx 20 \) defects, we have obtained their common optimal field amplitude, \( E_0 \approx 5 \) MV/cm, in several tens of iterations. In the present pulsed regime the temperature rises up to \( T \approx 3000 \) K, then it slowly relaxes, as the heat diffuses through the tubes, and is pumped out through the contacts. In the inset, we show the related broadening and reshaping of the temperature profile.

In Fig. 3, we show the probabilities \( p_i(t) \) of preparing structures with \( i \) defects, by application of the above three pulses separated by \( \mu \)s time periods. The pressure-induced coalescence leads to narrow population maxima at certain numbers of defects \( i \) after each pulse. The pulse creates less than \( D_i \) defects, before the pressure is temporarily released and the coalescence stops. When the pressure rises again, the process continues with the next pulse, until \( \langle N \rangle \approx 20 \) defects are created. In Fig. 4, we...
FIG. 4. Time-dependence of the average number of defects $\langle N \rangle$ (solid line) and their variance $\sigma_D$ (dashed line) for the pulsed excitation in Fig. 3. In the inset, we show the learning scheme used in optimal control of the welding process.

also present the time-dependence of the average number of defects $\langle N \rangle$ and the variance $\sigma_D$, for the excitation in Fig. 3. The simulation shows that $\langle N \rangle$ largely depends on the transferred energy, while $\sigma_D$ remains small, if $\langle N \rangle < D_1$ within one pulse.

In order to speed up formation of nanotube nets, we can consider simultaneous irradiation of many such junctions under a mask, which would concentrate the light on the selected spots. Tubular nets might be also prepared by self-assembly processes, if we succeed to initiate nanotube branching, i.e. splitting of their growth in orthogonal directions.

With more sophisticated light pulses [15–17] the method can also selectively catalyze chemical reactions inside or on the surfaces of nanotubes. This can lead to an efficient preparation of new hybrid materials, with on-site grown “filling” and “dressing”. An example is light-induced polymerization or growth of nanocrystals inside nanotubes [24]. The adaptive pulses could even control electronic processes in nanodevices, especially if the chemical constituents can be reversibly switched by light [25].

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