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Self-trapping nature of Tl nanoclusters on the Si(111)-7 × 7 surface

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Abstract. We have studied properties of thallium (Tl) nanoclusters formed on the Si(111)-7 × 7 surface at room temperature (RT) by utilizing photoemission spectroscopy (PES) and high-resolution electron-energy-loss spectroscopy (HREELS) combined with first principles calculations. Our PES data reveal that the surface states stemming from the Si substrate remain quite inert with Tl adsorption producing no Tl-induced state until saturation at Tl coverage \( \theta = 0.21 \) monolayers. Such a behavior, in sharp contrast with the extremely reactive surface states upon the formation of Na or Li nanoclusters, together with the presence of a unique Tl-induced loss peak in HREELS spectra suggests no strong Si–Tl bonding, and is well understood in terms of gradual filling of Si dangling bonds with increasing \( \theta \). Our calculation further indicates the presence of several metastable atomic structures of Tl nanoclusters at RT rapidly transforming from one to another faster than \( 10^{10} \) flippings per second. We thus conclude that the highly mobile Tl atoms form self-trapped nanoclusters within the attractive basins of the Si substrate at RT with several metastable phases. The mobile and multi-phased nature of Tl nanoclusters not only accounts for all the existing experimental observations available at present, but also provides an example of self-trapping of atoms in a nanometre-scale region.
1. Introduction

Metals on semiconductor surfaces have been intensively studied especially with a focus on some interesting features, such as metal-to-insulator transitions driven essentially by the enhanced many-body effects in reduced dimensional interacting electron systems [1]–[3]. Though the significant quantum confinement effect and the entanglement of exciton states due to the enhanced interaction at a few hundreds of nanometres scale has already been reported for such systems [4], we report here a case of metals on a semiconductor surface with a much reduced dimension of a few nanometres scale, where inter-atomic interactions appear to be quite unusual.

We find that nature allows trapping of several thallium (Tl) atoms into a region of nanometre scale in the form of a nanocluster on the Si(111)-7 \times 7 surface at room temperature (RT). Trapping of Tl atoms appears to be distinctly different from typical features of Tl–Si atomic bonding revealing a remarkably mobile character of Tl nanoclusters and significant inertness on substrate surface electronic states.

Because of its unique atomic arrangement of the unit cell consisting of a faulted half unit cell (FHUC) and an unfaulted half unit cell (UFHC) as depicted in figure 1, the Si(111)-7 \times 7 surface has been used as a fascinating template to fabricate a crystalline array of self-assembled nanoclusters of various atomic species. Most adsorbates upon forming nanoclusters are found to occupy highly symmetric sites around Si restatoms known as attractive basins (red circles in figure 1) [5]. Those nanoclusters formed on this surface at RT exhibit atomically well-resolved scanning tunneling microscopy (STM) images with six atoms in one or both half unit cells and appear to be semiconducting [6]–[8]. Tl nanoclusters, however, have been known to be exceptional to this trend showing fuzzy STM images and have been reported to be metallic [9]. It has been proposed that each Tl nanocluster contains nine mobile Tl atoms, instead of six as in most other nanoclusters, formed only in the FHUC to account for such distinct features of Tl nanoclusters [9, 10]. Moreover, studies on electronic band structures of most nanoclusters other than Tl suggest a strong chemical bonding between adsorbates and Si atoms accompanying significant displacement of central Si atoms by the adsorbates [11]–[13]. Such a strong chemical bonding may explain why the STM images of nanoclusters are so well resolved atomically for those nanoclusters except Tl nanoclusters.

Motivated by such peculiar features of Tl nanoclusters, we have investigated electronic and structural properties of Tl nanoclusters formed on the Si(111)-7 \times 7 surface by utilizing photoemission spectroscopy (PES) and high resolution electron energy loss spectroscopy (HREELS). We have also carried out first principles total energy calculations to estimate the thermal stability of an atomic arrangement of Tl nanoclusters at RT. We find that the substrate surface states, especially associated with Si restatoms, are quite inert to Tl adsorption until the
Figure 1. Structure of the Si(111)-7 × 7 unit cell. Several highly symmetric sites (red dots) around restatoms within the attractive basins (red circles) are possible binding sites of adsorbates [5].

completion of formation of nanoclusters in contrast to nanoclusters of other atomic species. Such a remarkable inertness of surface states together with an invisible semiconducting band gap in HREELS spectra suggest a distinctly weak chemical bonding between Tl and Si atoms. This also may eliminate a possibility of displacing an Si center adatom by Tl, which is often observed for most other nanoclusters formed on the Si(111)-7 × 7 surface. Our results of the first principles total energy calculation for several plausible atomic models of Tl nanoclusters, in fact, support such a scenario by revealing relatively small energy differences between different atomic models, and thus a significant hopping rate between different atomic configurations within the same attractive basin at RT. We find a ‘dynamic trapping state’ of Tl nanoclusters in the sense that a single Tl nanocluster consisting of nine Tl atoms is rapidly changing its atomic configuration due to low diffusion barriers between neighboring high-symmetry sites in the attractive basin while residing only in an FHUC. We present the experimental evidence and discuss the physical implication of the dynamic trapping state.

2. Experimental details

The PES chamber used to measure the valence band of our sample has a high-intensity He I discharge lamp (Omicron HIS-13) and a SPECs Phoibos-100 electron analyzer with an optimal resolution of 110 meV at RT. The HREELS system utilizes a Leybold–Heraeus ELS-22 spectrometer with an optimum resolution of 7 meV. Both the PES and the HREELS chambers equipped with several surface diagnostic probes including low energy electron diffraction (LEED) were maintained with a base pressure of less than 1 × 10^{-10} Torr during the entire course of measurements. We prepared our sample by using a highly doped n-type Si(111) wafer with a resistivity of 2 Ω cm. A Tl source was made by wrapping a small piece of Tl with a tungsten wire. We thoroughly degassed the sample and Tl source with the chamber pressure controlled under 3 × 10^{-10} Torr for several hours. The clean Si(111)-7 × 7 phase was obtained after cleaning the sample with a well-known recipe, i.e. heating up to 1200 °C for 10 s followed by annealing at 800 °C for about 5 min. The cleaned sample showing a well-defined
The 7 × 7 LEED pattern was then cooled to RT before depositing Tl. We first monitored the intensity variation of fractional-order LEED spots during continuous deposition of Tl atoms onto the clean Si(111)-7 × 7 surface at RT. The seventh-order LEED spots became sharper and stronger as Tl coverage θ increased and reached a maximum intensity at θ = 0.2 monolayers (ML) due to the constructive interference from a lattice-like array of Tl nanoclusters. For θ ≥ 0.21 ML, the spots became weaker and fuzzier with increasing coverage indicating an increasing disorder due to the extra Tl atoms added to the Tl nanoclusters [14]. Thus the completion of formation of a crystalline array of Tl nanoclusters on the Si(111)-7 × 7 surface was relatively easily detected by the local maximum in intensity of the (1/7 0) LEED spot at θc = 0.21 ML in agreement with the previous STM study [9].

### 3. Results and discussion

In figure 2, we present a progressive spectral change of the valence band of the Si(111)-7 × 7 surface at RT with increasing θ. The spectra were measured at an emission angle of 10° from the surface normal. One notes the well-defined surface states S1 and S2 from the clean Si(111)-7 × 7 surface at binding energies of 0.15 and 0.87 eV below the Fermi level. These states have been associated with central Si adatoms and Si restatoms, respectively, [15]. The contribution from corner Si adatoms has been reported to appear with a binding energy of 0.5 eV [15]. This contribution apparently is not well resolved at RT and renders the line shape of S1 asymmetric. The binding energy of the spectra in figure 2 has been corrected by taking the band-bending effect into account from the Si 2p core-level shift as a function of θ (see inset). We find that the bulk component of the Si 2p core-level remains unaffected by Tl adsorption until θc = 0.21 ML, where the array of Tl nanoclusters is best developed, and then begins to change rapidly with θ, exhibiting a band-bending effect due to a different chemical morphology from that of Tl nanoclusters.

We notice in figure 2 that the two surface states are not significantly affected by the Tl adsorption at the initial stage for θ ≤ 0.21 ML. This is especially true for S2, which is in sharp contrast with adsorption of other metal atoms, Li and Na, for example, where S2 disappears almost completely at a Na coverage as small as 0.03 ML [12, 13]. We also note that no new state associated with Tl appears until θ = 0.91 ML, where a new state N begins to show up. We recall that a new state appears for Na adsorption as early as at 0.03 ML [12, 13]. It is interesting to find, however, that adsorption of K shows a spectral change with K coverage quite similar to the one caused by Tl [16]. In order to examine the spectral changes more quantitatively, we have fitted the spectra with Gaussian peaks after subtracting the background with a polynomial function in the form of $f(x) = a(x - x_0) + b + c(x - x_0)^{-1} + d(x - x_0)^{-2} + e(x - x_0)^{-3}$.

We present our fit results in figure 3 for the states S2 in (a) and S1 in (b). Both states reveal remarkable spectral changes as coverage crosses θc = 0.21 ML as also seen from the structural changes in the previous STM study [9]. While the binding energy and the intensity of S2 changes gradually up to θc, they change more significantly for θ ≥ θc. Such a trend seems to be reversed for S1. More specifically, while the binding energy of S2 (S1) is increased by 20 (90) meV at θc, the intensity of S2 (S1) is decreased by 14 (50)%. Now we think of several plausible mechanisms to explain such spectral changes in figure 3. One may first consider the filling of the partially filled Si dangling bonds by a charge transfer from Tl atoms. Here, we assume no displacement of central Si adatoms by Tl, since no new surface state appears until at least θc = 0.21 ML. The partially filled S1 state pinning the Fermi
Figure 2. Progressive change of surface states S1 and S2 in photoemission spectra of the valence band as a function of Tl coverage $\theta$. The spectra were taken with a photon energy of 21.2 eV at an emission angle of 10° and their binding energy were corrected by Si 2p core-level shift shown in the inset. The surface states appear to be rather inert to Tl adsorption until $\theta_c = 0.21$ ML where Tl nanoclusters are spread uniformly throughout the surface. A new surface state (denoted as N) begins to show up at $\theta \geq 0.91$ ML.

level at 0.63 eV above the valence band maximum [17] becomes increasingly filled by the electrons from Tl atoms so as to make the state shift toward the higher binding energy side as observed in figure 3. Similar shifts have been reported also for the electron-doped bulk crystal or K-adsorbed graphene [18, 19]. The decreased intensity of S1 by 50% suggests the filling of the dangling bonds of central Si adatoms only in FHUC, which is consistent with earlier STM observation of Tl nanoclusters formed only in FHUC [9]. While S1 is affected significantly by the filling, the S2 state may remain inert as observed when the charge transfer is limited mainly to the central Si adatoms.
Figure 3. Changes of binding energy (navy dots) and intensity (purple dots) of surface state S2 (a) and S1 (b) extracted from PES data in figure 2 by fitting the spectra with Gaussian peaks after subtracting a polynomial background. The changes appear to be significantly different before and after $\theta_c = 0.21$ ML.

Another possibility to explain binding energy shifts of the surface states, especially for the remarkable binding energy shift of S1 state, is the effect driven by the enhanced inter-cluster interaction due to the reduced separation between neighboring nanoclusters with increasing $\theta$. Since we find several such examples showing the change in binding energy due to the enhanced inter-cluster interaction with reducing inter-cluster distance, we attribute the change of binding energy of S1 more than the filling effect to the enhanced inter-cluster interaction. We have, for example, explained the shift of Si 2p and Tl 5d binding energies with increasing $\theta$, while keeping the work function unchanged in terms of the enhanced inter-cluster interaction due to the reduced distance between nanoclusters [14]. El-Moghraby et al [20] showed in their calculation that the reduced inter-cluster separation results in lowering the ground-level energy due to the enhanced inter-cluster interaction. A similar trend has been reported also for the excitonic energies of quantum dots [4]. Since excitons are associated with electron–hole pair excitations, the enhanced excitonic energy produces a shift of the valence band so that the binding energy shift of the surface states S1 may be caused partly by the enhanced inter-cluster interaction with increasing $\theta$. Unfortunately we cannot quantify the amounts of the shifts due to this interaction at present since no relevant calculations are available. One may still think of the possibility that a new surface state may exist quite near the S1 and/or S2 states, but is hidden because of its weak intensity. Since the linewidths of both surface states remain almost...
Figure 4. (a) Progressive change of HREELS spectra with Tl coverage $\theta$. The spectra were obtained with a primary electron energy $E_p = 12$ eV at $2^\circ$ off from the specular direction. A unique loss peak L1 (b) of the clean Si(111)-7 $\times$ 7 surface and a Tl-induced L2 (c) are analyzed by fitting the spectra with Gaussian peaks. One notices that L2 shifts its loss energy toward higher energy with increasing $\theta$, while its intensity diminishes. No band gap is seen even after L2 is quenched completely at a coverage of 0.5 ML.

unchanged with $\theta$ up to 0.21 ML, however, we ruled out this possibility. The only visible new state associated with Tl adsorption appears for $\theta \geq 0.91$ ML as shown in figure 2.

Our HREELS data presented in figure 4 shows the spectral change with Tl adsorption. We have fitted the HREELS spectra for a quantitative analysis as done earlier [1, 21]. The spectral behavior turns out to be quite consistent with the explanation of our PES data based on the filling of dangling bonds of central Si adatoms. One first notices a Drude tail indicating the metallic nature of the clean Si(111)-7 $\times$ 7 surface. In figure 4(b), we also find a loss peak L1 of loss energy $E = 0.30$ eV observed only at an off-specular angle. Since the relatively broad linewidth ($\sim 160$ meV) of L1 and small electron concentration of a Tl nanocluster, we safely rule out the possibilities of a local vibrational origin and a plasmon. It certainly cannot be a phonon since the energy is higher than the highest optical phonon energy ($\sim 57$ meV) and no multiple phonon peaks are observed. We thus attribute L1 to an interband transition between states below and above the Fermi level of the Si(111)-7 $\times$ 7 surface.

The interesting feature we emphasize in figure 4 is the presence of a loss peak L2, which shifts toward higher loss energy while concomitantly losing its intensity. It disappears completely as shown by the featureless spectrum at $\theta = 0.5$ ML, when Tl nanoclusters no longer maintain their unique atomic arrangement due to the extra Tl atoms. Such spectral behavior of L2 may be easily understood considering the filling of dangling bonds of Si adatoms as for the binding energy shift of the S1 state in our PES spectra in figure 2. As the dangling bonds in the FHUC are gradually filled by the charge donation from Tl atoms with increasing $\theta$, the spectral intensity or density of states (DOS) decreases accordingly in the vicinity of the Fermi level.
Therefore, the metallicity of the surface gradually deteriorates by losing its dangling bonds due to Tl adsorption. Since the gradual loss of the metallicity causes the weight center of the S1 state shift toward the higher binding side as shown in figure 3, such a change in DOS near the Fermi level should show up as a loss peak L2 shifting toward higher loss energy with diminishing intensity as \( \theta \) increases. For \( \theta \gg \theta_c \), the DOS at the Fermi level becomes a noise level with S1 significantly quenched, which is consistent with the HREELS spectrum at \( \theta = 0.5 \) ML, where L2 disappeared completely. Since the Tl nanoclusters are formed only in the FHUC, the surface does not show a band gap due to the remaining dangling bonds in the UHUC even though it is completely covered with Tl nanoclusters in the FHUC at 0.20 ML.

In order to confirm our explanation for the experimental observations discussed above, we have carried out first principles density function calculations using an \textit{ab initio} plane wave pseudo-potential method (VASP code) in conjunction with projector-augmented wave potentials within the generalized-gradient approximation (GGA) \cite{22,23}. The calculation employs a plane wave-basis set with an energy cut-off of 250 eV for a single \( k \) point in the Brillouin zone. The unit cell in the slab model consists of 9 Tl and 12 Si adatoms in addition to six layers of Si and 49 H atoms passivating Si dangling bonds in the bottom layer.

As a first step to find the most stable atomic structure of a Tl nanocluster, we have calculated the adsorption energy for several high-symmetry sites in the attractive basin (see inset in figure 5). Details of calculational results will appear elsewhere \cite{24}. The bridge site \( B_2 \) in an FHUC is found to be the most stable with an adsorption energy \( E_a = -2.36 \) eV atom\(^{-1} \) favored over the same site in the UHUC of \( E_a = -2.30 \) eV atom\(^{-1} \). When the second (third) Tl atom is placed at another bridge site around a neighboring restatom, \( E_a \) is decreased by 0.008 (0.01) eV atom\(^{-1} \) indicating attractive interaction between Tl atoms within the FHUC.

Therefore, a nanocluster begins to form only in FHUCs by this attractive interaction between Tl atoms as observed in the STM study \cite{9}. On the other hand, when three atoms of Al (Ga) are adsorbed at on-top sites (\( T_4 \)) on Si atoms in the second layer, the most favored position for single Al (Ga) atom adsorption, \( E_a \) is increased by 0.14(0.01) eV atom\(^{-1} \) \cite{25}. Because of the repulsive interaction between the first two Al (Ga) atoms, Al (Ga) nanoclusters are formed in both the half unit cells as observed also in previous STM studies \cite{26,27}.

Although the STM image of the surface with Tl nanoclusters best developed at 0.21 ML appears fuzzy, Pb nanoclusters having about similar atomic mass or In nanoclusters belonging to the same elemental group exhibit atomically well-resolved STM images. One may notice that the Pb and In nanoclusters are formed with central Si adatoms significantly displaced by adsorbate atoms \cite{6,8}. For Tl nanoclusters, no evidence of such a substrate reconstruction is found in PES or in HREELS data since no new surface state induced by Tl is seen in PES spectra, nor has any loss peak associated with Tl indicating a strong chemical bonding been observed. Zotov et al \cite{10} reported, however, that the Tl adsorbed surface revealed several stable atomic structures depending on \( \theta \) when annealed at a mild temperature, which showed well-resolved STM images. Therefore, the surface with Tl nanoclusters at RT is a metastable surface, where Tl nanoclusters are thought to be quite mobile to produce such fuzzy STM images \cite{9}. Such a mobile nature of Tl nanoclusters has also been suggested by our earlier x-ray study, thus proposing a dynamical model where four different atomic configurations of Tl nanoclusters coexist at RT \cite{28}.

With this background, we have calculated the hopping rate of Tl atoms to estimate the mobility at RT for eight different atomic structures depicted in figure 5. Possible structures other than those eight models are ruled out since occupation of bridge sites is favored over other...
Figure 5. Total energy of eight different plausible atomic configurations (from a to g) of Tl nanoclusters formed in FHUC have been calculated to estimate the thermal stability of Tl nanoclusters at RT. Several highly symmetric sites (B$_2$, B$_2'$: bridge, H$_3$: hollow, T$_4$: on-top, and T$_1$: atop) around a restatom are denoted as red circles in the inset. Tl atoms, Si restatoms and Si adatoms in the first layer are denoted by red, yellow and blue circles, respectively, while Si atoms in the second layers are denoted by green circles.

high-symmetry sites, for example, the on-top or hollow sites (H$_3$) by 0.07 and 0.10 eV atom$^{-1}$, respectively. We assumed no reconstruction of substrate surface or replacement of Si atoms with adsorbates and each Tl nanocluster contains nine Tl atoms as indicated by the coverage of 0.21 ML, 9 Tl atoms on 49 Si atoms, for the fully developed Tl nanoclusters in FHUCs. The total energy difference calculated for the eight structures is presented in figure 6. One finds that the differences among the structures are less than 0.10 eV atom$^{-1}$. The small total energy differences among eight possible structures strongly suggest a dynamical model proposed by the x-ray study [28].

In order to estimate the hopping rate of Tl atoms between high-symmetry sites, we assumed the half unit cell of the Si(111)-7 × 7 surface as a potential well with a lateral length of 26.8 Å considering the Si dimers as the boundary of the well. This assumption is based on the fact that Si dimers constituting the boundary of the unit cell are found to be the most unstable adsorption sites for metal atoms [5].

As an example of the hopping process, we have considered two processes shown in figure 7, where the stable Tl atoms occupying a B$_2$ site initially move to another stable site B$_2'$ by overcoming the energy barriers $E_d = 0.07$ eV at a T$_4$ site and $E_d = 0.10$ eV at an H$_3$ site. To calculate the hopping rate $\nu$, we adopted the equation $\nu = v_0 \exp(-E_d / k_B T)$, where...
Figure 6. Difference in total energy per Tl atom of the eight atomic configurations shown in figure 5. One notes that the maximum total energy difference among the configurations is not greater than 0.10 eV.

Figure 7. Two possible hopping paths of Tl atoms from bridge site B₂ to another bridge site B₂′ through (a) B₂ → T₄ → B₂′ and (b) B₂ → H₃ → B₂′ paths. The energy barriers at on-top site (T₄) and at hollow site (H₃) are 0.07 and 0.10 eV, respectively. Tl atoms, Si restatoms, Si adatoms in the first layer and Si atoms in the second layer are denoted by red, yellow, blue and green circles, respectively.

ν₀ is the attempt frequency, Eₐ the energy barrier, kₜ is Boltzmann’s constant and T is the sample temperature. The attempt frequency ν₀ defined as a colliding frequency of atoms with the energy barrier has been evaluated for Pb, Y and Ag atoms within the half unit cell as 5 × 10⁹ hoppings s⁻¹ [29]. In the calculation by Vasco et al, they assumed no hoppings between attractive basins for the convenience of calculation. We note that this value of ν₀ on the Si(111)-7 × 7 surface is smaller than the typical values on metal surfaces of 10¹¹–10¹³ hoppings s⁻¹ [29]. Since ν₀ depends on the width of a potential well w, we have used ν₀ = 7 × 10¹¹ hoppings s⁻¹ because of the reduced width w = 2.2 Å between the two bridge sites within a single attractive basin with barriers at T₄ or H₃ sites. We thus obtain ν = 4 × 10¹⁰ hoppings s⁻¹ for the upper
path $B_2 \rightarrow T_4 \rightarrow B'_2$ in figure 7 and $10^{10}$ hoppings s$^{-1}$ for the lower path $B_2 \rightarrow H_3 \rightarrow B'_2$ at RT. Such significant values of the hopping rate of Tl atoms clearly indicate that the Tl nanoclusters are quite mobile at RT. Their hopping, however, is restricted within the same attractive basin of the FHUC because of the much higher energy barriers between the basins and between the neighboring FHUCs [5, 7]. Considering the average scanning frequency of 0.25 scans s$^{-1}$ for STM measurements of a half unit cell [30], the fuzzy STM images of Tl nanoclusters can be caused by such high hopping rates between several metal-stable atomic configurations as also suggested by the recent x-ray study [28]. We thus confirm that Tl nanoclusters formed on the Si(111)-7 × 7 surface are quite mobile to rapidly transform their atomic configurations at RT and show no strong bonding between Tl and substrate Si atoms. The Tl nanoclusters, therefore, provide an example of self-trapping of a nanocluster in nature within a region as small as a nanometre scale.

4. Summary

We have measured electronic properties of a crystalline array of Tl nanoclusters formed on the Si(111)-7 × 7 surface at RT. The valence band PES data show no Tl-induced surface state while intrinsic Si surface states S1 and S2 remain relatively inert until a Tl coverage of 0.21 ML, where Tl nanoclusters cover all FHUCs on the surface. Such a behavior of Si surface states is in sharp contrast with nanoclusters of other atomic species, such as Na or Li nanoclusters, where they are rapidly quenched at an early stage of adsorption. No band gap is observed and a characteristic loss peak associated with Tl adsorption in HREELS data shifts toward the higher loss energy side with gradually decreasing spectral intensity as Tl nanoclusters are formed. All these experimental data are understood in terms of the filling of dangling bonds stemming from Si adatoms. Inter-cluster interaction also seems to play a role in driving the additional shift of the S1 state. Our theoretical calculation is found to support our explanation based on the filling of dangling bonds and further suggests that the Tl nanoclusters are quite mobile and transform their atomic arrangements by hopping through rather shallow energy barriers between high-symmetry binding sites with a rate faster than $10^{10}$ hoppings s$^{-1}$ at RT. We thus conclude that Tl atoms form nanoclusters that are self-trapped in FHUCs and highly mobile within FHUCs with several different structural phases at RT. These unique features of Tl nanoclusters and the absence of strong Tl–Si bonding account for all the experimental data not only discussed here, but also other available observations such as the puzzling fuzzy STM images and a dynamical mixing model proposed by an x-ray study. The system of Tl nanoclusters self-trapped in potential wells of nanometre scale, i.e. within FHUCs of the Si(111)-7 × 7 surface, at RT may thus be a good candidate to study Rabi oscillation for several quantum dot arrays or to explore the possibility of quantum qubits for highly dense optical devices [31].

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