A robust nitridation technique for fabrication of disordered superconducting TiN thin films featuring phase slip events

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Disorder induced phase slip (PS) events appearing in the current voltage characteristics (IVCs) are reported for two-dimensional TiN thin films produced by a robust substrate mediated nitridation technique. Here, high temperature annealing of Ti/Si3N4 based metal/substrate assembly is the key to produce majority phase TiN accompanied by TiSi2 & elemental Si as minority phases. The method itself introduces different level of disorder intrinsically by tuning the amount of the non-superconducting minority phases that are controlled by annealing temperature (Ta) and the film thickness. The superconducting critical temperature (Tc) strongly depends on Ta and the maximum Tc obtained from the demonstrated technique is about 4.8 K for the thickness range ~ 12 nm and above. Besides, the dynamics of IVCs get modulated by the appearance of intermediately resistive steps for decreased Ta and the steps get more prominent for reduced thickness. Further, the deviation in the temperature dependent critical current (Ic) from the Ginzburg–Landau theoretical limit varies strongly with the thickness. Finally, the Ta intermediate resistive steps in the IVCs and the depairing current are observed to alter in a similar fashion with Ta and the thickness indicating the robustness of the synthesis process to fabricate disordered nitride-based superconductor.

Disordered superconductors have exhibited various fundamental quantum phenomena like superconductor–insulator transition (SIT)1,2, quantum criticality3,4, quantum phase slip (QPS)5 etc. Of particular interest, disordered superconductors are suitable for phase slip (PS) study6 which may lead to interesting applications in single photon detection and quantum current metrology7. The PS mechanism, which relates to a change in time for superconducting order parameter due to phase fluctuations, plays a crucial role for the survival of superconductivity in reduced dimension7. Further, the physical mechanism of dissipation in superconductors is associated with PS process8. For example, in 1D superconducting nanowire, the phase of the order parameter fluctuates continuously and the phase fluctuations lead to vanishing order parameter momentarily when the phase slips by 2π and thus making the wire resistive at the phase slip centers (PSCs). This is known as PS phenomenon which can be initiated by applied current for a current carrying superconductor9.

Analogous to PSCs in 1D, phase fluctuations lead to phase slip lines (PSLs) in wide 2D superconducting films that exhibit resistive steps in current–voltage characteristics (IVCs)10. Experimentally PSSs can be triggered by magnetic doping11,12, embedding artificial pinning centers13 or by using magnetic field14. Here, we address the effects of disorder on the dynamics of IVCs for quasi 2D TiN thin films. In recent years, ultrathin TiN films have been reported to exhibit SIT14, quantum criticality14 and Berezinskii–Kosterlitz–Thouless (BKT) transition15. Further, it has been reported that disordered TiN can be a promising candidate for QPS study16,17. Here, we report the formation of PSLs by observation of staircase-like structures appearing in the IVCs for disordered TiN thin films. We demonstrate that by tuning the disorder the superconducting-to-normal state transition in the measured IVCs changes from a single step transition to a transition embedded with multiple steps featuring the formation of PSLs. The tuning of disorder level in TiN films has been achieved by adopting a novel substrate mediated nitridation technique18,19, which employs high temperature annealing of Ti/Si3N4 based metal/.

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substrate assembly to prepare majority phase TiN thin films accompanied by TiSi₂ and elemental Si as minority phases¹⁸. Conventionally, TiN films are grown either by using reactive dc sputtering of Ti in presence of Ar/N₂ gas mixtures²¹⁻²³ or by atomic layer deposition²⁴⁻²⁵ in presence of N₂ gas etc.²⁶⁻³¹. However, a fine tuning of nitrogen concentration is needed to achieve the stoichiometric highly crystalline fcc TiN known to possess higher superconducting critical temperature ($T_c$).

By using this substrate mediated nitridation technique, we have produced 3–20 nm thick TiN films with $T_c$ ranging from 3.0 to 4.8 K, respectively, and the results are comparable to the best reported values²¹⁻²⁷,²⁹ Here, we address the effects of $T_a$ and film thickness on the superconducting properties of TiN thin films. The maximum $T_c$ obtained is around 4.8 K for the film with thickness 20 nm and annealed at 820 °C. $T_a$ decreases with the decrease in $T_c$ & film thickness. Further, the formation of PSLs and their evolution in the IVCs have been studied under the application of external fields. Finally, we have investigated the effects of $T_a$ and film thickness on the temperature dependent critical current ($I_c$) by using Ginzburg–Landau (GL) theory³² and we have found that the $I_c$ and the PSLs vary in a similar fashion with $T_c$ and the film thickness.

Results and discussion

The temperature dependent resistance ($R(T)$) measurements on thin films-based samples are presented in Fig. 1. The device configuration in conventional four probe measurement scheme for a representative sample is shown in the inset of Fig. 1a. The width of the film is around 500 μm and the distance between the two voltage leads is around 1.1 mm. A set of zero field $R(T)$, measured on the batch of 12 nm thick samples annealed at different $T_a$, is presented in Fig. 1a. During the course of $R(T)$ measurements from room temperature to 2 K, the samples undergo normal (NM) to superconducting (SC) phase transition which strongly depends on $T_a$. It is evident from Fig. 1a that the NM-SC transition shifts towards lower temperature for lower values of $T_a$. For example, the highest $T_c$ appears for $T_a = 820$ °C, whereas, we do not observe any transition down to 2 K for the sample annealed at 650 °C. The various critical temperatures are defined in Fig. 1b which displays the thickness dependent $R(T)$ data for samples annealed at 820 °C. Here, the film thickness varies from 20 to 3 nm. The $T_c$ is defined as the temperature at which the derivative $dR/dT$ becomes maximum, which is shown by the dashed vertical line in Fig. 1b for the representative sample of thickness 3 nm. The maximum $T_c$ of about 4.8 K is obtained for the sample TN1 of 20 nm thickness. With thickness decreasing from 20 to 12 nm as that for sample TN2, the $T_c$ is reduced to 4.76 K indicating a very little change or saturation in $T_c$ for the films with thickness ≥ 12 nm. With further reduction in the film thickness, $T_c$ reduces from that of the maximum $T_c$ of TN1 (~ 20 nm) by 0.4 K, 1.2 K and 1.8 K for samples TN3 (~8 nm), TN4 (~4 nm) and TN5 (~3 nm), respectively. This implies that the effect of film thickness on $T_c$ becomes prominent for the thickness around 10 nm and below. The reduction in film thickness increases the normal state resistance ($R_n$). Initially, the change in $R_n$ from 20 nm (27.6 Ω) to 12 nm (68.6 Ω) is more than 3 times. With further decreasing thickness, $R_n$ increases to more than 5.5 times for 8 nm (154 Ω), 11.8 times for 4 nm (327 Ω) and 27.8 times for 3 nm (769 Ω) with respect to 20 nm thick sample. However, the change in $R_n$ with respect to $T_a$ is shown in Fig. 1a, is apparently random and will be discussed later.

Further, we have collected the $T_c^{Onset}$ and $T_c^{Zero}$ values for samples with various thickness for $T_a$ equal to 820 °C, 780 °C and 750 °C and those are displayed with respect to thickness in Fig. 1c. For $T_a = 820$ °C and 780 °C, $T_c$ strongly depends on thickness in the lower thickness regime (thickness ~ 4 nm and lower), whereas, for $T_a = 750$ °C, the variation in the $T_c$ with thickness is very little and the same is marked by the dotted circle. The overall variation of the $T_c$ on $T_a$ and film thickness is displayed by color plot in Fig. 1d which is divided into several zones. Based on the increasing order of the $T_c$, the regimes I-to-IV are separated from each other. Regime-I, the lowest $T_c$ regime, corresponds to a very little change of about 0.1 K in $T_c$ with thickness in the range of 4 nm and below for $T_a < 780$ °C. In comparison with regime-I, regime-II is noticeably different. Here, for $T_a > 780$ °C, $T_c$ remains almost unchanged for a very narrow thickness range, whereas, for $T_a < 780$ °C, a wide span of thickness delivers almost the same $T_c$. Hence in regime-II, the $T_c$ shows strong dependence on thickness for higher $T_a$. In regime-III, the effect of increased $T_a$ or increased thickness results in same direction towards increasing $T_c$. Finally, the highest $T_c$ zone regime-IV is originated mainly from higher $T_a$ (≥ 780 °C) and here, the $T_c$ is observed to saturate for increased thickness. However, for the case of higher film thickness (~ 4 nm and above), the $T_c$ strongly varies with $T_a$ from 3.12 to 4.76 K. Therefore, $T_a$ plays a significant role in changing the $T_c$ ranging from 4.76 K for 820 °C to no transition down to 2 K for 650 °C for 12 nm thick films. Apart from the $T_{Onset}$, the influence of $T_a$ is also observed on $R_n$ as already evident in Fig. 1a. Here, $R_n$ reduces with decreasing $T_a$ from 820 to 750 °C and further reduction in $T_a$ leads to increased $R_n$. Unlike $T_c$, the dependence of $R_n$ on $T_a$ is not straightforward and that is mainly due to the presence of minority phases like TiSi₂ and Si that are generated and modulated by the annealing process³⁸. Here, $R_n$ varies in the range between 60–87 Ω for 12 nm thick TiN film, which is lower than that of TiSi₂ and Si, the substrate remains as elemental Si which in turn contribute to the increased resistance in the normal state³⁸. However, the change in $R_n$ with respect to thickness [Fig. 1b] is much more than the change due to the variations.
in \( T_\text{c} \) [Fig. 1a]. For comparison, we have presented \( R_g \) with respect to \( T_\text{c} \) and thickness by using 3-D color plots in Fig. 2d. It is apparent that \( R_g \) is mainly dominated by the thickness variations.

Finally, from Figs. 1, 2, we have demonstrated the variation of \( T_\text{c} \) & \( R_g \) with thickness & \( T_a \) for disordered TiN thin films accompanied by nonsuperconducting minority phases of TiSi\(_2\) and Si\(^{18}\). As \( T_a \) plays a huge role in the decomposition of Si\(_3\)N\(_4\) and diffusion of Si & N elements inside the film\(^{18}\), the influential role of \( T_a \) on particularly the superconducting properties of TiN thin films is also confirmed by the present study. It is noteworthy to mention that the achieved best \( T_\text{c} \) by employing the current synthesis technique can be comparable, and some cases can be even better than, the reported conventional methods [Table S1 in the Supplementary Information (SI)].

So far, we have discussed the influence of film thickness & \( T_a \) on \( T_\text{c} \) and \( R_g \). Now, we consider the effect of film thickness and \( T_a \) on the IVCs for samples prepared under different growth conditions. In Fig. 3, we display IVCs of three selective samples, namely, TN4, TN8 & TN12, that are annealed at 820 °C, 780 °C & 750 °C, respectively. Each of these selected samples are of 4 nm thickness which is less than their respective coherence length \( \xi(0) \) [Fig. S5 in SI]. This indicates that the samples are in the 2D limit, where phase fluctuations lead to PSLs\(^{35}\) and IVCs exhibit resistive steps\(^{36,37}\). In Fig. 3a, we display a set of zero field \( R(T) \) measured on the aforementioned three representative samples. Similar to Fig. 1a, here also we observe a shifting of the NM-SC phase transition towards lower temperature for reduced \( T_a \). For example, \( T_c \) changes from 3.6 K for sample TN4 (~ 820 °C) to...
3.12 K for sample TN8 (~780 °C) to 2.5 K for sample TN12 (~750 °C). However, very little variation in \( R_n \) is observed among the samples. First, we present the IVC isotherms for sample TN4 in Fig. 3b which shows a single step sharp switching during the phase transition from the superconducting-to-metallic state at temperature far below the \( T_c \). The current at which the switching occurs is known as the critical current (\( I_c \)), whereas, the current corresponding to the onset of superconducting state from the normal state during the downward sweeping direction is defined as the retrapping current (\( I_r \)) [Fig. S6 in SI]. For all the measured samples, these two characteristic currents are different and the IVCs appear to be hysteretic with respect to the current sweeping direction. With increasing temperature, the hysteresis reduces and finally vanishes at \( T_c \) as shown in Fig. S6 in SI. Hysteretic IVCs are commonly observed in granular superconducting films due to the Joule heating effect, which locally increases the effective temperature and hence reduces the \( I_c \) [38,39]. Further, at temperatures close to the \( T_c \), intermediate resistive steps start to appear at 3.0 K and higher temperature as highlighted by the red dotted arrows in Fig. 3b. The slopes of these resistive states increase in the increasing current direction and they converge at one single point [the grey dotted lines], known as the excess current \( I_s \). These characteristics indicate that the intermediate resistive states originate due to PSLs [8,11]. Besides, the intermediate resistive steps become more prominent for the sample TN8 as shown in Fig. 3c. A single sharp switching is observed at 2.4 K and below but the sudden emergence of intermediate resistive steps takes place for the isotherms measured at 2.5–2.8 K. Further, black dotted lines connecting the slopes of each resistive steps meet at a single point on the current axis at \( I_s \) confirming the formation of PSLs in disordered TiN thin films. These intermediate resistive steps get more prominent even at lower temperature for the sample TN12 as shown in Fig. 3d. Here, the resistive states exist for much wider extent in current indicating the reduced \( T_c \) indeed play a favorable role in support of PSL formation.

Reduction in thickness introduces more disorder [14–17] as that is also evident in the increased \( R_n \) presented in Figs. 1b and 2d. However, relating disorder directly to the resistivity would not be appropriate in the present scenario as there are secondary phases present along with TiN. Here, the disorder is related mainly to the granularity and the grain size of the films as the surface morphology studied by SEM and AFM [Fig. S1–S3 in the SI] suggests

**Figure 2.** Core-level XPS binding energy spectra of (a) Ti 2p, (b) N 1 s and (c) Si 2p for reference samples annealed with varying annealing temperatures. The XPS spectra were taken from inside the films after removing the top surface by Ar+ ion sputtering at 500 eV for about 2 min. (d) Variation in the \( R_n \) with the variations in \( T_n \) and thickness of the films.
the variations in the grain size with sample thickness. Generally, granular superconductors can be considered as an array of Josephson junctions where superconducting grains act as the superconducting islands and the grain boundaries serve as the weak-links and the macroscopic superconductivity is established by superconducting proximity effect. However, the establishment of macroscopic coherence depends strongly on the grain size and the inter-granular distance. Further, the intergranular region is very important as it contributes to the disorder by possessing any impurity like the presence of Si and the silicide phases, oxygen content, Ti residual layer etc. Here, for the thinner samples with much smaller grain size, the effect of grain boundaries, intergranular distance, the content and/or type of the intergranular region contribute significantly to the disorder as compared to that of the thicker samples.

In order to examine the effect of disorder on IVCs, we have studied more samples with reduced thickness and varying $T_a$. In Fig. 4, we present IVCs for two such samples TN5 and TN9 that are annealed at 820 °C & 780 °C, respectively. The samples from the 3 nm thickness batch. Here for sample TN5 with $T_a = 820$ °C in Fig. 4a, the intermediate resistive steps during the SC-to-NM transition become much more prominent and wide compared to that for 4 nm thick sample TN4 presented in Fig. 3b. Initially, IVC isotherms show almost single step transition for measurement temperature 2.3 K and below, whereas, for temperature above 2.3 K, the single step transition is converted into a multiple step transition from superconducting state to metallic state. Furthermore, compared to TN5, intermediate resistive steps get even more pronounced and broad for sample TN9, which was annealed at 780 °C as shown in the Fig. 4b. Unlike the sample TN8 annealed at 780 °C with thickness 4 nm presented in
Fig. 3c, wide resistive states start to show up even at 2 K base temperature for TN9. These resistive steps are a signature of the formation of PSLs occurring due to the annihilation of vortex-antivortex pairs emerging from the edges of the films. Therefore, both $T_a$ & film thickness play crucial roles in altering the emergence of intermediate resistive steps in IVCs, however, the effect of film thickness is more prominent than that of $T_a$ as the former introduces more disorder than the later.

In order to examine the effect of magnetic field on the IVCs of these disordered TiN thin film samples, we have selected two samples, TN4 and TN5, that were annealed at $T_a = 820 \degree C$ but of thickness 4 nm and 3 nm, respectively. Here, IVCs were measured at varying magnetic field while keeping the measurement temperature unaltered. For sample TN4, the field dependent IVCs measured at 2.7 K are presented in Fig. 5a which shows a single step transition from SC-to-NM state from 0–25 mT. With a further increase in the field up to 50 mT, an intermediate resistive step starts to appear in the course of the SC-to-NM transition instead of a single step transition. Here, the resistive step gets narrower in extent with increasing field and the same remains prominent up to 250 mT. With further increasing field, the intermediate step starts to diminish and the SC-NM transition gets smoother. Furthermore, the evolution of the intermediate resistive step with magnetic field has been displayed by the contour color plot in Fig. 5b with the support of the differential resistance ($dV/dI$) extracted from the measured field dependent IVCs. Considering the range of magnetic field within which the intermediate step appears, the contour plot in Fig. 5b is confined within 300 mT. Here, because of the single step transition, the differential resistance is maximum at 0–25 mT, whereas at higher fields, it gets reduced by the introduction of intermediate resistive steps that are indicated by the presence of multiple peaks at a particular field during the SC-NM transition. However, at 250 mT and above, presence of a single, and relatively stronger peak, in the $dV/dI$ indicates the removal of intermediate steps by the external magnetic field. In Fig. 5b, the position corresponding to the peak of $dV/dI$ at a particular magnetic field relates to the $I_c$ which reduces as the field moves towards the higher side. As observed in Fig. 4, reduction in film thickness makes the intermediate resistive steps more prominent. In order to examine the effect of field on reduced film thickness, we have measured field dependent IVCs for the sample TN5 with thickness 3 nm at the measurement temperature 2.3 K and the same is exhibited in Fig. 5c. Here, the zero field IVC shows no intermediate steps but the steps start to emerge at 25 mT and remain prominent up to 175 mT. It is to be noted that with reduction in thickness from 4 to 3 nm, the number of intermediate steps increases indicating a greater number of transition segments in the SC-NM phase transition region. The same is evident by the appearance of multiple peaks in the concerned differential resistance $dV/dI$ representation through the colour plot in Fig. 5d. From Fig. 5c,d, initially the intermediate steps get wider with increasing field up to about 100 mT and with further increasing field in the range between 125–175 mT, the wide steps start to break up into a greater number of steps. The splitting of the steps is clearly evident by the presence of multiple low-amplitude $dV/dI$ peaks encircled by the dotted region in Fig. 5d. Furthermore, intermediate sharp resistive steps start to disappear at 200 mT and there is a gradual increase in voltage from superconducting to normal state with a very little variation in differential resistance.

Further, we have extracted the critical current ($I_c$) and retrapping current ($I_r$) from the IVCs at zero field for five representative samples TN4, TN5, TN8, TN9 and TN12. Already, we have presented the effect of $T_a$ and film thickness on the IVCs of disordered TiN thin films in Figs. 3 and 4. Here, we show the influence of $T_a$ and film thickness on the temperature dependent $I_c$ & $I_r$. We have investigated the temperature dependence of $I_c$ in the light of Ginzburg- Landau (GL) theory and modified GL theory whereas, the $I_r$ has been explained by the existing hotspot model given by Skocpol, Beasley, and Tinkham (SBT). We have found that the theoretical GL...
The equation $I_c \propto (1 - t)^s$; with $s' = 3/2$ is valid near the $T_c$ to explain the temperature dependent $I_c$, and it deviates at temperature far below the $T_c$ ($T < 0.75T_c$) as shown by the blue dotted curves in Fig. 6a,b,d for samples TN4, TN8 and TN5, respectively. In order to fit entire range of measured temperature points, we have adopted the modified GL Eq. $I_c \propto (1 - t^2)^{s}(1 + t^2)^{1/2}$, where we use the exponent $s'$ as the free parameter to have the best fit to the experimental data. The red solid curves represent the best fits using the aforementioned modified GL equation for the samples presented in Fig. 6a,b,d with the exponent values 1.32, 1.35 and 1.70, respectively. The acquired exponent ($s$) values from the fitting are close to the theoretical value of exponent around 1.5. However, the difference of about 0.03 in the exponent $s$, for the samples with same thickness of 4 nm (TN4 & TN8), is negligible compared to the difference of about 0.35 for the sample TN5 of 3 nm thickness with the samples having thickness of 4 nm (TN4 or TN8). Further, for samples TN12 [Fig. 6c] and TN9 [Fig. 6e], the measured temperature varies within 0.75$T_c$ and $T_c$, and we obtain the best fits (the solid blue curves) using the GL equation, where the exponent $s'$ is used as a free parameter. Here, the values for the exponent $s'$ from the fits are 1.31 and 1.83 for TN12 and TN9, respectively. The exponent for the sample TN12 of 4 nm thickness is close to the theoretical value and also is similar to the other 4 nm thick samples TN4 &TN8. However, the deviation in the exponent for the sample TN9 with thickness of 3 nm from the theoretical value is more and is on the higher side. Furthermore, the fits from two other 3 nm samples, TN5 & TN9, thickness have offered exponent values that are very close to each other. Therefore, it is evident from the above critical current analysis that the thickness, and hence, the disorder plays a significant role in controlling the temperature dependent $I_c$ in wide disordered superconducting thin films. Here, we observed that the exponent values, as obtained from the fits for 4 nm thick samples (TN4, TN8, TN12) are of the same order and lower than the theoretical value and 3 nm thick samples (TN5&TN9) have exponent values much higher than the theoretical value of 1.5. The higher exponent is mainly due to the presence of higher level of disorder in thinner samples. Apart from $I_c$, we have

![Figure 5.](#) Magnetic field dependence of IVCs for samples TN4 (~ 4 nm) and TN5 (~ 3 nm) that are annealed at 820 °C. (a) Field-dependent IVCs for sample TN4 measured at fixed temperature 2.7 K and (b) corresponding dV/dI with respect to field & current in 3-D colour plot. (c) Variation of IVCs with magnetic field but at fixed temperature 2.3 K for sample TN5 and (d) the related dV/dI with respect to field & current in 3-D representation using contour colour plot. The Black solid arrows and dotted arrows in (a,c) indicate the increasing direction of applied magnetic field and the current sweeping direction, respectively.
measured the temperature dependent $I_r$ for all the above five samples and the collection of those is presented in Fig. 6f. First, we observe that the amplitude of $I_r$ reduces with the reduction in $T_a$ for the samples having same thickness. Similarly, reduction in thickness also reduces the $I_r$ for samples annealed at same $T_a$. Therefore, $I_c$ and $I_r$ follow the similar trend as that of $T_c$ with the variations in thickness and $T_a$. In the present case due to hysteretic IVCs, $I_c$ and $I_r$ are different and this is mainly due to the Joule heating in the resistive state. Therefore, we have used the SBT hotspot model using equation, $I_r \propto (1-t) s^r$, to fit the retrapping current. Here, $s^r = 1/2$ is the theoretical value. The best fitted colored curves, using the exponent $s^r$ as a free parameter, are presented in Fig. 6f for individual samples. The exponent for the samples TN4 ($s^r = 0.46$), TN8 ($s^r = 0.44$) & TN12 ($s^r = 0.42$) are close to the theoretical value of 0.5, whereas, there is a small deviation from the theoretical value for the sample TN5 ($s^r = 0.37$) and a further deviation appears for TN9 ($s^r = 0.23$). The deviation in exponent values from the theoretical value increases with decreasing $T_a$ and reduction in thickness indicating the influence of disorder on the mechanism of depairing current limit. Finally, the influence of $T_a$ and film thickness on the $I_c$ and $I_r$ is reflected by the various exponent values used to explain and understand the experimental results by using the existing models. The measured colored lines represent the fitted curves by using eqn. $I_r \propto (1-t) s^r$.
the temperature dependent critical current from its theoretical value. Therefore, the enhanced level of disorder due to the reduction in film thickness plays a very important role in monitoring the superconducting properties and the overall SC-NM phase transition.

### Conclusion

In conclusion, we have fabricated disordered superconducting TiN thin films by establishing an unconventional but robust, nitridation method which involves high temperature annealing of Ti thin films deposited on Si₃N₄/ Si substrates. The annealing process leads to the decomposition of Si₃N₄ into N and Si atoms that form majority TiN and minority TiSi₂ phases by reacting with Ti₁₈. Generally, disorder is present in pure thin films and here the presence of TiSi₂ and excess Si can further enhance the level of disorder. The best obtained \( T_c \) among the measured samples is \( \sim 4.8 \) K for film thickness of about 12 nm and above. As expected, \( T_c \) plays a very important role in tuning the \( T_c \). We also show that the \( T_c \) and \( R_n \) depend strongly on the film thickness. Furthermore, the IVCs for ultrathin (≤ 4 nm) samples feature staircase-like steps indicating the appearance of PSLs that evolve more prominently with the reduction in thickness and by external magnetic fields. Finally, the \( T_c \) achieved by using this technique is comparable to the best reported values in the literature (Table S1). Other superconducting parameters are summarized in Table 1. Furthermore, the \( T_c \), PSLs and the temperature dependent critical current vary in a similar fashion on the growth parameters like \( T_a \) and the thickness.

### Methods

**Material synthesis through a novel technique.** We used undoped intrinsic Si (100) substrate covered with 80 nm Si₃N₄ dielectric spacer layer, grown by low pressure chemical vapor deposition (LPCVD), as the substrate for the growth of TiN films. The substrates were cleaned by using the standard cleaning process involving sonication in acetone and isopropanol bath for 15 min each, followed by oxygen plasma cleaning of 10 min. Thereafter cleaned samples were loaded into the sputtering unit and transferred to ultra-high vacuum (UHV) chamber where they were pre-heated at about 820 °C for 30 min under very high vacuum conditions (\( p \approx 5 \times 10^{-6} \) Torr) in order to remove any adsorbed or trapped molecules/residue on the surface of the substrate. After performing all the cleaning process, cleaned Si₃N₄/Si substrate was cooled down to room temperature and transferred to the sputtering chamber through load lock without breaking the vacuum. A thin layer of Ti was then deposited on the substrate by dc magnetron sputtering of Ti (99.9995% purity) in the presence of high purity Ar (99.9999%) gas. Sputtering of Ti was performed with a base pressure less than 1.5 \( \times 10^{-7} \) Torr. Finally, the sputtered sample was transferred again into the UHV chamber for post-sputtering annealing. Ti films on Si₃N₄/Si (100) were annealed at different annealing temperatures (~820 °C, ~780 °C, ~750 °C, ~700 °C and ~650 °C) for 2 h at a pressure less than 5 \( \times 10^{-8} \) Torr. The thickness values for the films are determined by the optimized rate and thickness measurements on various samples prepared with same deposition time. The average value obtained from the thickness measurements is assigned to the thickness and the errors represent the range of variations on the measured values. Here, variation in annealing temperature is within ± 10 °C. During the annealing process, Si₃N₄ decomposes into Si and N atoms and due to high affinity of titanium towards both nitrogen and

| Samples | \( T_a \) (°C) ± 10 °C | \( d_0 \) (nm) | \( T_c \) (K) | \( \Delta T \) (K) | \( \xi(0) \) (nm) | \( R_n \) (6 K) \( \mu \Omega \text{cm} \) | RRR = \( R_n (6 K)/R_n (300 K) \) | \( \rho_n (6 K), (\mu \Omega \text{cm}) \) | Intermediate steps in IVCs @ zero-field |
|---------|-----------------|-------------|-------------|----------------|-----------------|----------------|-----------------|-----------------|----------------|
| TN1     | 820 ± 2         | 4.8         | 0.2         | –              | 47              | 1.70           | 34.5            | –               | Majorly single step transition |
| TN2     | 820 ± 1         | 4.76        | 0.2         | 9.5            | 140             | 1.61           | 65              | –               | Majorly single step transition |
| TN3     | 820 ± 1         | 4.4         | 0.25        | –              | 214             | 1.39           | 77              | –               | Majorly single step transition |
| TN4     | 820 ± 0.8       | 3.6         | 0.23        | 8.7            | 408             | 1.24           | 82              | Single step transition |
| TN5     | 800 ± 0.5       | 3.0         | 0.32        | 7.94           | 879             | 1.14           | 135             | Multiple step transition |
| TN6     | 820 ± 0.9       | 2.0         | 0.25        | –              | 25,742          | 0.70           | 4588            | –               | Multiple step transition |
| TN7     | 780 ± 12        | 4.38        | 0.18        | 10.8           | 98              | 1.54           | 47              | Single step transition |
| TN8     | 780 ± 0.8       | 3.12        | 0.26        | 9.2            | 370             | 1.21           | 75              | Multiple step transition |
| TN9     | 780 ± 0.5       | 2.5         | 0.28        | 9.0            | 808             | 1.10           | 127             | Multiple step transition |
| TN10    | 780 ± 0.5       | 2.0         | 0.25        | –              | 2650            | 0.98           | 338             | –               | Multiple step transition |
| TN11    | 750 ± 12        | 3.52        | 0.3         | 9.6            | 83              | 1.38           | 45              | Single step transition |
| TN12    | 750 ± 0.8       | 2.5         | 0.27        | 10             | 383             | 1.18           | 81              | Multiple step transition |
| TN13    | 750 ± 0.5       | 2.4         | 0.29        | –              | 851             | 1.10           | 133             | –               | Multiple step transition |
| TN14    | 700 ± 12        | 2.0         | 0.25        | –              | 99              | 1.24           | 60              | –               | Multiple step transition |
| TN15    | 700 ± 0.8       | –           | –           | –              | 473             | 1.08           | 109             | –               | Multiple step transition |
| TN16    | 650 ± 12        | –           | –           | –              | 200             | 1.10           | 136             | –               | Multiple step transition |

*Table 1. Superconducting parameters obtained for TiN thin films fabricated by using the substrate mediated nitridation technique.*
silicon, stable stoichiometric cubic titanium nitride (TiN) forms as a majority phase along with the minority phases such a titanium silicide (TiSi₂) and elemental silicon (Si). Here, temperature plays an important role to control the chemical kinetics happening during the chemical reaction because phenomena like decomposition and diffusion are very much sensitive to temperature. Therefore, concentration of majority and minority phases varies with the annealing temperatures (T_a) such as for T_a > 780 °C, majority phase is accompanied by elemental Si rather than silicide phase, whereas for T_a ≤ 780 °C, it is accompanied by silicide phase. The concentration of silicide phase is maximum for T_a ~ 780 °C and the same gets reduced with the decrease in T_a.

For structural characterization we fabricated thin films on substrates with an area of 5 mm x 5 mm. For the transport measurements, we have patterned the thin films into Hall bar geometry by using shadow mask made of stainless steel. We have used a complimentary separate mask to make the contact leads for voltage and currents probes. The device geometry for a representative device is shown in the inset of Fig. 1a. The contact leads were made of Au (~ 50 nm)/Ti (~ 5 nm) deposited by dc magnetron sputtering.

**Structural characterizations.** Photoelectron Spectroscopic (XPS) measurements were performed in UHV based Multiprobe Surface Analysis System (Thermo Scientific Nexsa) operating at a base pressure of 1.5 x 10⁻⁷ Pa. A monochromatic Al-Kα radiation source (1486.7 eV) was employed with radiation spot size of 400 μm for the excitation. To enhance the sampling depth and minimize the contribution of native oxides & contaminants, in-situ sputtering via energetic Ar⁺ ions (at 500 eV) was performed for about 2 min. The depth profile scan was taken in “snapshot mode” in order to reduce the data acquisition time at the expense of spectra resolution. The adventitious carbon C–C bond at 284.8 eV was used for binding energy correction.

**Morphological characterizations.** The morphological characterizations of the samples were performed by using scanning electron microscope (Gemini SEM 500 ZEISS) and atomic force microscope (AFM) from BRUKER, Dimension ICON, in tapping mode.

**Low temperature temperature measurements.** Transport measurements were carried out using a 16 T/2 K Physical Properties Measurement System (PPMS) of Quantum Design, USA at UGC-DAE CSR Indore.

**Data availability**

The data that represent the results in this paper and the data that support the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions
S.Y. and S.S. fabricated the devices. S.Y., V.K., M.P.S., V.G. and R.P.A. carried out the low temperature transport measurements. S.Y. and S.S. analyzed the data and S.Y. wrote the manuscript. S.S. planned, designed and supervised the project. All the authors read and reviewed the manuscript.

Competing interests
The authors declare no competing interests.

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