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**Titanium hydride formation in Ti/Pt films:
the impact on Ti/Pt/Au-gated III-V FETs**

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Abstract — Ti/Pt metal layers are an integral part of the gate stack of many III-V field-effect transistors (FETs). These devices are known to be affected by H₂ exposure. In this study, Auger Electron Spectroscopy (AES) measurements of Ti/Pt bilayers are correlated with electrical measurements of InAlAs/InGaAs/InP FETs fabricated with Ti/Pt/Au gates. The FET measurements show that H₂ exposure shifts the device threshold voltage through the piezoelectric effect. AES reveals the formation of titanium hydride (TiH_x) in Ti/Pt bilayers after identical H₂ exposures. These results indicate that the volume expansion associated with TiH_x formation causes compressive stress in Ti/Pt/Au gates, leading to the piezoelectric effect. After a subsequent recovery anneal in N₂, the FET measurements show that V_T recovers. AES measurements confirm that the TiH_x in hydrogenated Ti/Pt bilayers also decreases after further annealing in N₂.

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Hydrogen sensitivity of III-V field-effect transistors (FET) is a well documented and serious reliability concern [1-3]. The most common gate metallization for devices intended for operation in the millimeter-wave regime is Ti/Pt/Au. Electrical studies have shown that both Pt and Ti play a key role in H₂ sensitivity [1-3]. Pt is known to be a catalyst for H₂, breaking it down into 2H, which diffuses through the gate [4]. Previous studies have linked this mechanism to hydrogen passivation of donors [4]. Hydrogen-induced degradation, however, has also been documented in FETs fabricated with Ti-only gates [2]. This lead to speculation that hydrogen exposure causes a change in the Schottky barrier of the gate (ϕ_B) due to the formation of titanium hydride [2]. However, recent results have shown that the changes in device characteristics exhibit a gate length and orientation dependence, which cannot be explained by a change in ϕ_B , but instead display characteristics typical of a piezoelectric effect [3]. It has been postulated that the formation of TiH_x produces compressive stress in the Ti layer, and tensile stress in the underlying semiconductor. This stress changes the FET characteristics through piezoelectric-induced polarization charges in the semiconductor [3]. Similar orientation-dependent changes in device characteristic have been observed in FETs with stressed dielectric over-layers [5-7].

This study uses Auger Electron Spectroscopy (AES) to directly examine the effects of hydrogen exposure on Ti/Pt bilayers. Hydrogen cannot be detected directly because of its light atomic weight. Using AES, hydrogen can be detected indirectly through its effects on the valence band density of states and on the energies of core levels in Ti when TiH_x is formed. In this work, AES results are correlated with electrical measurements of FETs fabricated with Ti/Pt/Au gates, and confirm that the presence of TiH_x in Ti/Pt layers is associated with piezoelectric-induced changes in FET characteristics.

Two types of test structures were used in this study. The first structures were lattice-matched InAlAs/InGaAs modulation-doped FETs fabricated on InP substrates, and were used for electrical measurements. The details of the FET structure and fabrication are found in [3]. The FET gate metallization was 250Å Ti/ 250Å Pt/ 3000Å Au, deposited by e-beam evaporation. The transistor gate lengths varied from 0.8 μm to 10 μm. On a (100) substrate, devices with gates oriented along the [011], [010] and [01 $\bar{1}$] direction were characterized.

The second test structures were 250Å Ti/ 250Å Pt bilayers deposited on 4" Si wafers which were coated with 1450Å of LPCVD Si₃N₄. These samples were used for AES measurements. The Auger spectra were collected with a cylindrical mirror analyzer using a primary beam energy of 2 keV and a signal modulation voltage of 2 V. The measurement system used a rastered beam to avoid problems associated with surface decomposition after prolonged electron bombardment. Argon ion sputtering was used to obtain composition profiles of the structure.

Prior to testing, the FET samples underwent a thermal burn-in at 230°C in pure N₂ until any changes in device characteristics due to thermal processing were saturated. The device threshold voltage, V_T, was used to monitor hydrogen-induced degradation. V_T was measured *in situ* during degradation.

Hydrogen exposure for both electrical and AES measurement samples occurred in a wafer probe-station equipped with a heated chuck and a sealed chamber which allowed the introduction of an ambient gas. The samples were annealed at 200°C for up to 3 hours in forming-gas (5% H₂ in N₂). Control samples were annealed in pure N₂ under identical conditions. Following the degradation anneal, some samples underwent a subsequent recovery anneal in pure N₂ for 15 hrs.

The results of the *in situ* FET measurements during the forming-gas anneal are shown in Fig. 1a. The V_T is proportional to \sqrt{t} , suggesting that this is a diffusion-limited process. The changes in V_T exhibit gate-length and orientation dependencies, which are key signatures of the piezoelectric effect [5-7]. This indicates that stress is playing a role in device degradation during hydrogen exposure. Previously reported orientation-dependent changes in device characteristics have been attributed to stress from the dielectric over-layer [5-7]. However, we have seen nearly identical results on devices with no dielectric over-layer, showing that the gate is the source of the stress.

Fig. 1b shows the change in V_T observed during the recovery anneal in pure N₂. Observing the short gate-length devices, we find that the V_T shift is largely recoverable after a subsequent anneal in N₂ at 200°C for 15 hrs. The recovery behavior is also proportional to \sqrt{t} , suggesting that it is also diffusion-limited.

The results of the Auger analysis performed on Ti/Pt bilayers are presented in Fig. 2, which shows the Auger spectra in the Ti layer, 150Å from the Ti/Pt interface. Relative to the N₂ control sample, the sample annealed in forming-gas shows a +1 eV shift in the low-energy Ti peak, and the emergence of a prominent, hydrogen-induced peak 5 eV below the main peak. These are the characteristic signatures of titanium hydride [8]. We have focused on the low-energy (26 eV) Ti peak because, unlike the other main Ti peaks, this region is not affected by the presence of Ti-O or Ti-N bondings [9, 10]. Thus, this spectral region is a fingerprint for TiH_x formation [8].

Also shown in Fig. 2 is the Auger spectra obtained from hydrogenated Ti/Pt bilayers which underwent a subsequent recovery anneal in pure N₂ at 200°C for 15 hrs. Following the recovery anneal, the H-induced peak nearly disappeared. These results are consistent with recovery of ΔV_T observed in FET electrical measurements.

Fig. 3 shows the depth profile of the Auger spectra in the Ti layer for hydrogenated Ti/Pt samples. The spectra obtained near the Ti/Pt interface show a large h-induced peak and the full +1 eV shift in the main Ti peak. This indicates that the TiH_x is nearly stoichiometric [8]. The decrease in the H-induced peak intensity as we approach the Si₃N₄/Ti interface indicates that the hydrogen concentration in the TiH_x decreases [9].

To show more clearly the evolution of hydride composition through the layer, in Fig. 4 we plot the ratio of the H-induced peak intensity to the total (Ti + H-induced) peak intensities as a function of distance into the Ti layer. The nearly stoichiometric compositions exist only close to the Ti/Pt interface. The hydride composition becomes increasingly non-stoichiometric as we approach the Si₃N₄/Ti interface.

Fig. 4 also shows the results obtained from Ti/Pt samples which were subjected to a subsequent recovery anneal in pure N₂ at 200°C for 15 hr. After the recovery anneal, the hydride remains only in the upper regions of the Ti layer near the Ti/Pt interface. Thus it appears that the stoichiometric hydrides are more stable and remain after the N₂ recovery anneal, and the non-stoichiometric hydrides decompose.

The phase diagram of the Ti-H system shows that the equilibrium system at 200°C for low to moderate concentrations of hydrogen consists of an α -solution of H in Ti, and a hydride phase [11]. This hydride phase is normally f.c.c. with a percent volume increase, $\Delta v/v$, of 21% [12]. However, Numakura showed that at very low at. % of hydrogen (< 20%), hydride precipitates form which have an f.c.t. structure, with $\Delta v/v$ of 15% [13, 14]. This f.c.t. titanium hydride is similar to the γ -phase f.c.t. hydride precipitate found in the Zr-H system, which is considered to be metastable because it converts to an f.c.c. structure upon aging [12, 13]. In contrast to this, the f.c.t. hydride in the Ti-H system does not revert to the f.c.c. structure upon aging [13]. This is most likely because of the larger volume increase of the f.c.c. structure, making its formation more difficult. Nevertheless, the f.c.t. titanium hydride is still considered to be a metastable phase which forms only at very low H concentrations [13]. In our experiment, the presence of stable, nearly stoichiometric hydrides near the Ti/Pt interface indicates that the hydrides in this region may have an f.c.c. structure.

In conclusion, we find that the formation of metastable hydride precipitates can affect the characteristics of FETs which use Ti/Pt films in the gate structure. AES analysis has confirmed that titanium hydride, believed to be mainly in the form of metastable f.c.t. precipitates, forms in Ti/Pt bilayers after exposure to low concentrations of hydrogen. The volume increase associated with the formation of TiH_x leads to compressive stress in the Ti film. Consistent with this, hydrogen-induced shifts in the threshold voltage of FETs with Ti/Pt/Au gates are found to arise from the piezoelectric effect due to stress in the gate. After subsequent anneals in pure N_2 , the amount of TiH_x detected by AES in hydrogenated Ti/Pt bilayers decreases. Electrical measurements show that the magnitude of the V_T shift observed in FETs also decreases after a N_2 recovery anneal. These findings should be instrumental in identifying a device level solution to this problem.

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REFERENCES

1. W.O. Camp, Jr., R. Lasater, V. Genova and R. Hume, "Hydrogen effects on reliability of GaAs MMICs," *IEEE GaAs IC Symp.*, p. 203, 1989.
2. P.C. Chao, W. Hu, H. DeOrion, A.W. Swanson, W. Hoffmann, and W. Taft, "Ti-gate metal induced PHEMT degradation in hydrogen," *IEEE Elec. Dev. Lett.*, v. 18, n. 9, p. 441, 1997.
3. R.R. Blanchard, J.A. del Alamo, P.C. Chao and S.B. Adams, "Hydrogen degradation of InP HEMTs," *Proc. of IEDM*, p. 231, 1998.
4. K. Christmann, G. Ertl, and T. Pignet, "Adsorption of hydrogen on a Pt (111) surface," *Surf. Sci.*, v. 54, p. 365, 1976.
5. C.-P. Lee, R. Zucca and B.M. Welch, "Orientation effect on planar GaAs Schottky barrier field effect transistors," *Appl. Phys. Lett.*, v. 37, p. 311, 1980.
6. N. Yokoyama, H. Onodera, T. Osnishi and A. Shibatomi, "Orientation effect of self-aligned source/drain planar GaAs Schottky barrier field-effect transistors," *Appl. Phys. Lett.*, v. 42, p. 270 (1983).
7. P.M. Asbeck, C.-P. Lee and M.F. Chang, "Piezoelectric effects in GaAs FET's and their role in orientation-dependent device characteristics," *IEEE Trans. Elec. Dev.*, v. ED-31, n. 10, p. 1377, 1984.
8. B.C. Lamartine, T.W. Haas and J.S. Salomon, "Characterization of TiH_x and TiD_{0.9} surfaces: AES, ELS, SIMS and XPS studies," *Appl. Surf. Sci.*, v. 4, p. 537, 1980.
9. P. Bracconi and R. Lässer, "Investigation of titanium and titanium hydride by AES and EELS," *Appl. Surf. Sci.*, v. 28, p. 204, 1987.
10. P.J. Basset and T.E. Gallon, "The effect of oxidation on the high resolution Auger spectrum of titanium," *J. of Elec. Spect. and relat. Phen.*, v. 2, p. 101, 1974.
11. W. M. Mueller, "Titanium Hydride," in *Hydrogen in Metals III*, G. Alefeld and J. Völkl, eds. Springer-Verlag, 1978.
12. R.L. Beck and W.M. Mueller, in *Metal Hydrides*, edited by W.M. Mueller, J.P. Blackledge and G.G. Libowitz, Academic Press, New York, 1968.

13. H. Numakura and M. Koiwa, "Hydride precipitation in titanium," *Acta metall.*, v. 12, p. 1799, 1984.
14. H. Numakura, M. Koiwa, H. Asano, H. Murata and F. Izumi, "X-ray diffraction study on the formation of γ titanium hydride," *Scripta Metallurgica*, v. 20, p. 213, 1986.

Captions:

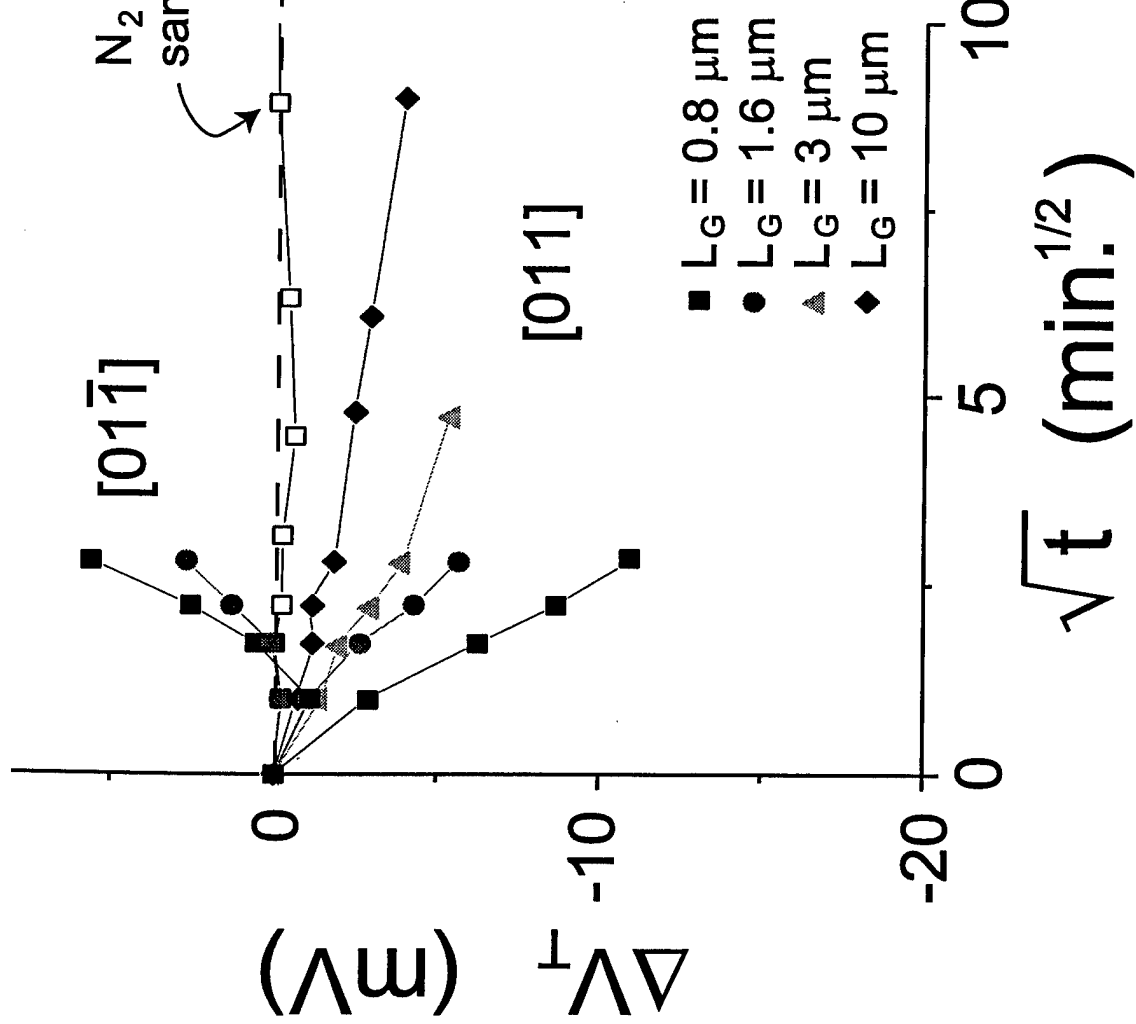
Fig. 1: Shift in FET threshold voltage, ΔV_T , measured *in situ* (a) during the anneal in forming-gas at 200°C, and (b) during the subsequent recovery anneal in N₂ at 200°C. Orientation dependence of ΔV_T during forming-gas anneal is a key signature of the piezoelectric effect, indicating stress in the gate metal. Control samples annealed in N₂ shown in open symbols.

Fig 2.: AES measurement of Ti/Pt bilayers. Spectra obtained in Ti (150Å from the Ti/Pt interface) after annealing in either N₂ or forming-gas at 200°C for 1 hrs. The +1 eV shift in the low energy (26 eV) Ti peak, and the emergence of a H-induced peak 5 eV below the main peak, are the characteristic signature of TiH_x. After a subsequent recovery anneal in pure N₂, the H-induced peak nearly disappears.

Fig. 3: Depth profile of Auger spectra in the Ti layer of Ti/Pt bilayers. The large H-induced peaks in spectra obtained near Ti/Pt interface indicate near stoichiometric compositions of TiH_x. The hydrogen content in the hydrides decreases with increasing depth into the Ti layer.

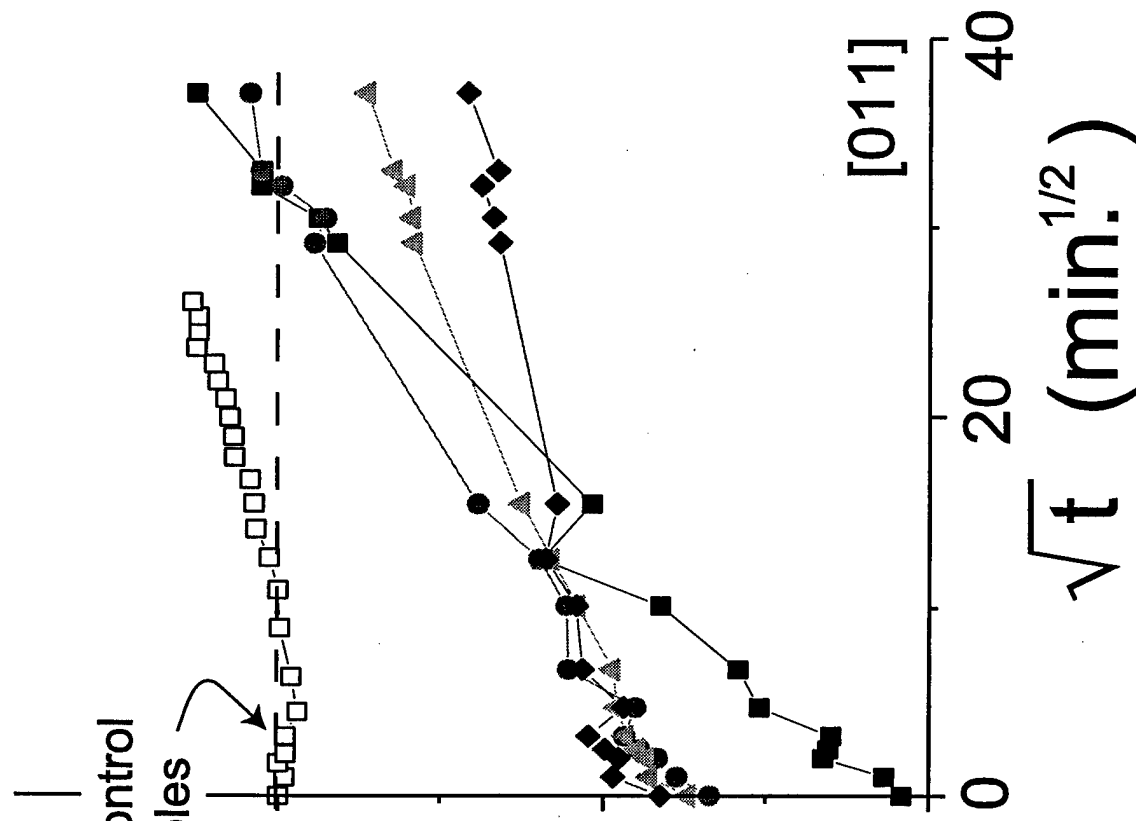
Fig. 4: Plot of the ratio of the H-induced peak intensity to the total peak intensities (Ti-peak + H-induced peak), as a function of depth into the Ti layer. Solid line indicates profile obtained after forming-gas anneal at 200°C for 1 hrs. Dashed line indicates the profile obtained after a subsequent recovery anneal in pure N₂ at 200°C for 15 hrs.

forming-gas anneal
200°C



(a)

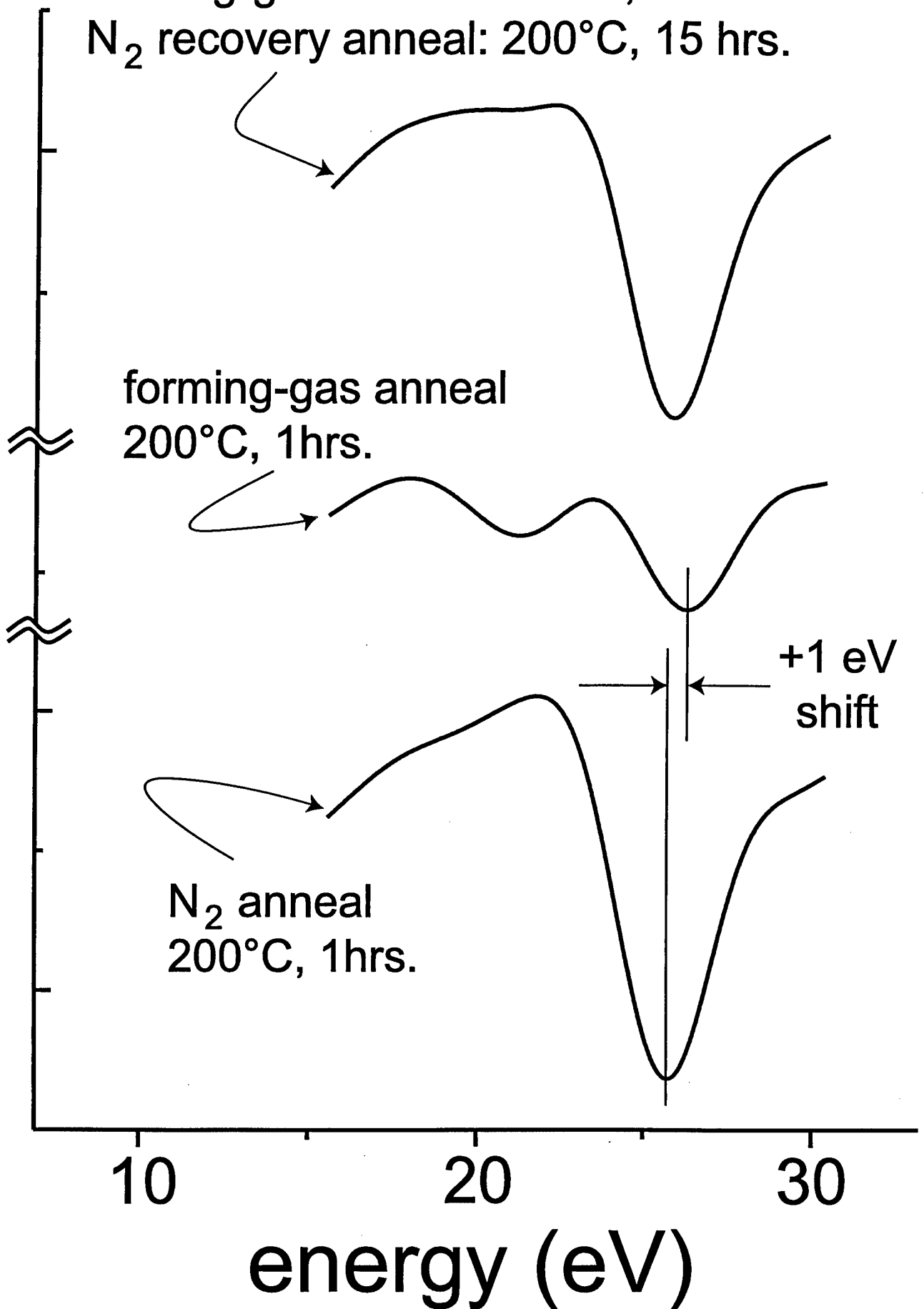
N₂ recovery anneal
200°C

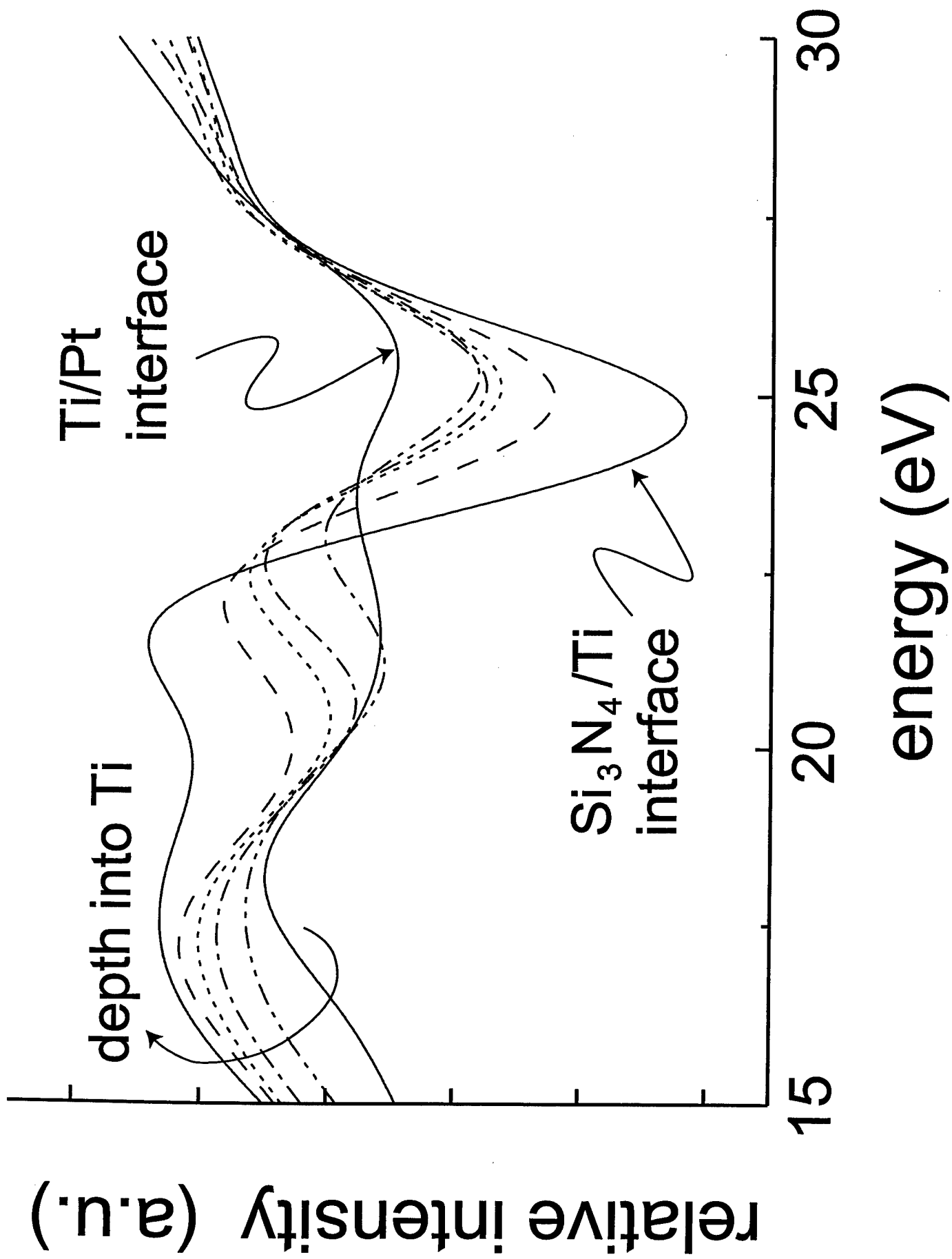


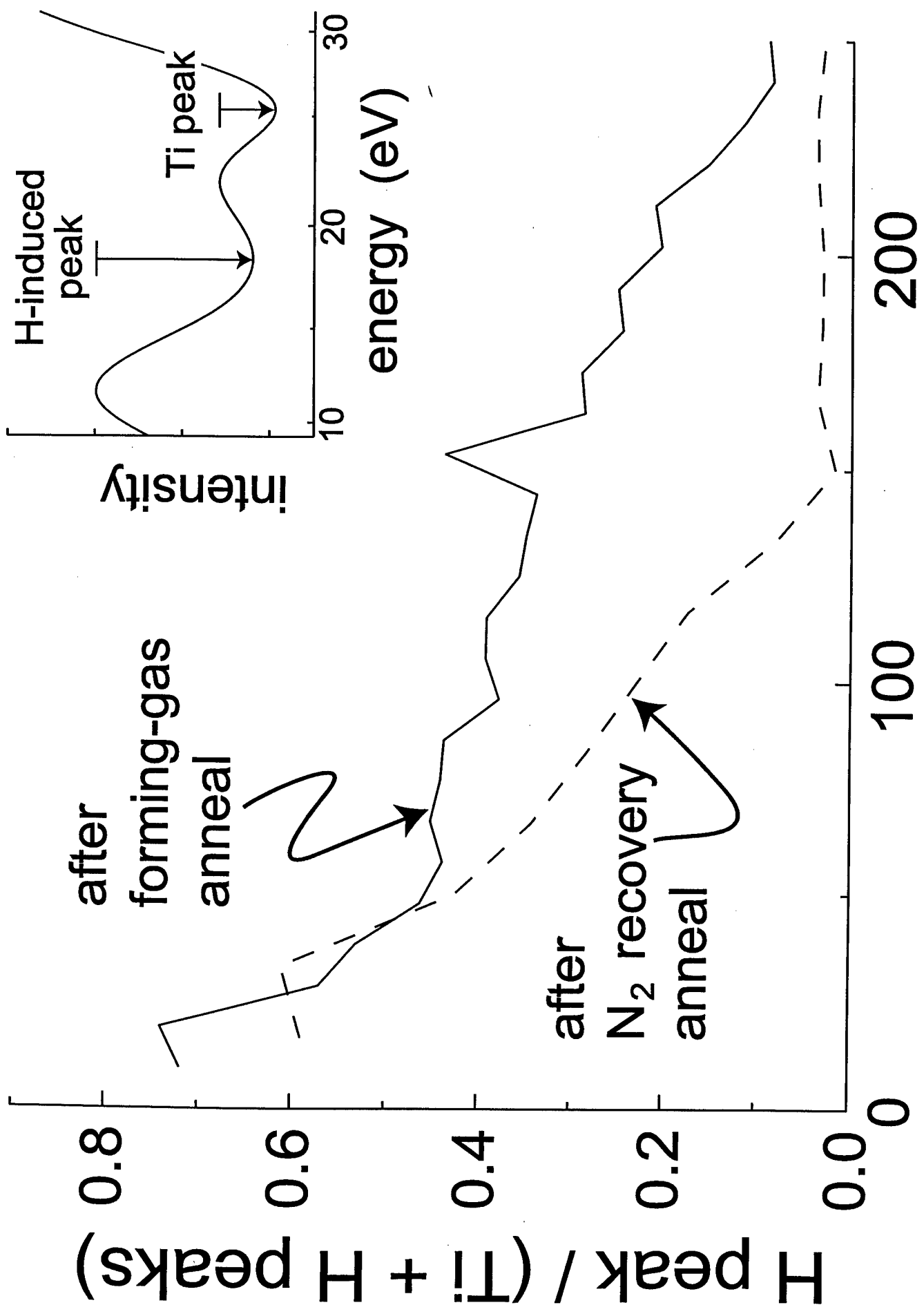
(b)

relative intensity (a.u.)

forming-gas anneal: 200°C, 1hrs.
N₂ recovery anneal: 200°C, 15 hrs.







distance from Ti/Pt interface (Å)