2

OFFICE OF NAVAL RESEARCH

Grant N00014-91-J-1550

R&T Code: 413w003

Technical Report No. 14

Competitive pairing and the chemistry of coadsorbed hydrogen and halogens on Ge(100)

by

Y. L. Yang, S. M. Cohen, and M. P. D'Evelyn

Prepared for publication in

Materials Research Society Symposium Proceedings

Rice University
Department of Chemistry
Houston, TX 77251-1892

December 11, 1992

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE December 1992	3. REPORT TYPE AND DATES COVERED Technical

4. TITLE AND SUBTITLE

Competitive pairing and the chemistry of coadsorbed
hydrogen and halogens on Ge(100)

5. FUNDING NUMBERS

Grant #:
N00014-91-J-1550

6. AUTHOR(S)

Y. L. Yang, S. M. Cohen, and M. P. D'Evelyn

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Rice University
Department of Chemistry
Houston, TX 77251-1892

8. PERFORMING ORGANIZATION REPORT NUMBER

Technical Report
#14

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

Prepared for publication in:
Materials Research Society Symposium Proceedings

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The chemistry of coadsorbed H and X (X=Cl, Br) on semiconductor surfaces is important in epitaxial growth of silicon from chlorosilanes and of Si_xGe_{1-x} alloys, in hydrogenating/halogenating cycles in atomic layer epitaxy, and also provides an interesting model system, yet has received little attention to date. We have investigated the interaction of HCl and HBr with Ge(100) by temperature-programmed desorption, and find that H_2, HCl and HBr each desorb with near-first-order kinetics near 570-590 K and that $GeCl_2$ and $GeBr_2$ desorb with near-second-order kinetics near 675 K and 710 K, respectively. Analysis of the desorption kinetics of H_2 and HX leads to the conclusion that adsorbed H and X atoms pair preferentially in a qualitatively similar way as H atoms adsorbed alone on Ge(100)2×1 or Si(100)2×1 and that pairing of H+X occurs in competition with pairing of H+H.

14. SUBJECT TERMS

Germanium, hydrogen, pairing, HCl, HBr, surface chemistry, kinetics

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT

NSN 7540-01-280-5500

Standard Form 298 (Rev 2-89)
Prescribed by ANSI Std Z39-18
298-102

COMPETITIVE PAIRING AND THE CHEMISTRY OF COADSORBED HYDROGEN AND HALOGENS ON GE(100)

YUEMEI L. YANG, STEPHEN M. COHEN, AND MARK P. D'EVELYN
Department of Chemistry and Rice Quantum Institute, Rice University, Houston, TX
77251-1892

ABSTRACT

The chemistry of coadsorbed H and X (X=Cl, Br) on semiconductor surfaces is important in epitaxial growth of silicon from chlorosilanes and of Si_xGe_{1-x} alloys, in hydrogenating/ halogenating cycles in atomic layer epitaxy, and also provides an interesting model system, yet has received little attention to date. We have investigated the interaction of HCl and HBr with Ge(100) by temperature-programmed desorption, and find that H_2, HCl and HBr each desorb with near-first-order kinetics near 570-590 K and that $GeCl_2$ and $GeBr_2$ desorb with near-second-order kinetics near 675 K and 710 K, respectively. Analysis of the desorption kinetics of H_2 and HX leads to the conclusion that adsorbed H and X atoms pair preferentially in a qualitatively similar way as H atoms adsorbed alone on Ge(100)2×1 or Si(100)2×1 and that pairing of H+X occurs in competition with pairing of H+H.

INTRODUCTION

Chlorosilane chemical vapor deposition (CVD), which involves surface hydrogen and chlorine as intermediates, has been the dominant epitaxial silicon growth technology for twenty years, yet the current state of understanding of the behavior of coadsorbed hydrogen and halogens on semiconductor surfaces is rather primitive. Hydrogen-halogen surface chemistry is also of critical importance to the development of methods for atomic layer epitaxy of the group IV materials diamond, silicon, and germanium, where one atomic layer is deposited per cycle of alternating fluxes of a chlorinated precursor and molecular or atomic hydrogen.[1,2] Progress has made in recent work on the adsorption and decomposition of chlorosilanes on silicon surfaces,[3,4] but the hydrogen halides constitute a more basic model adsorption system for understanding the properties of coadsorbed hydrogen and halogen atoms.

In this paper we report results from a temperature-programmed desorption (TPD) investigation of the interaction of HCl and HBr with Ge(100), with emphasis on the desorption kinetics of H_2, HCl, and HBr.

EXPERIMENTAL

Experiments were performed in an ultrahigh vacuum chamber[5] (base pressure = $1\text{-}2 \times 10^{-10}$ Torr), pumped via a liquid-N_2-trapped diffusion pump and titanium sublimation pump, and equipped with LEED/ESDIAD optics, an Auger spectrometer, infrared optics, a quadrupole mass spectrometer (QMS) with a water-cooled shroud, a calibrated gas doser,[6] and an ion gun.

A Ge(100) sample (Si-Tech, Inc.), cut 4–6° off the (100) plane towards the [011] direction, 0.25–0.30 mm thick, n-type, ρ = 5–40 Ω cm, was cut into a rectangle 13.4 mm × 13.8 mm. A chromel-alumel thermocouple was cemented into a small hole drilled near one edge using Aremco

☑
☐
☐

:es

A-1

Mater. Res. Soc. Symp. Proc. (in press)

516 high-temperature cement. The sample was mounted between Ta-foil clips attached to a Cu block and could be heated resistively to above 873 K and cooled with liquid nitrogen down to 153 K. The active area presented to the doser after mounting was 11.5 mm × 13.4 mm. After degreasing, the Ge sample was placed in the chamber, and cleaned by several sputter-and-anneal cycles ($i_{Ar^+} = 2$–$3\ \mu A\ cm^{-2}$, $E_{Ar^+} = 500\ V$, $T_{anneal} = 850\ K$).

HCl or HBr exposures were performed by rotating the sample to face the doser and admitting a known amount of gas to the chamber through a calibrated aperture. Computer calculations of flux[7] show that, for this sample geometry, 17 % of the molecules leaving the doser hit the sample, yielding a flux of $(4.11 \pm 0.23) \times 10^{15}\ M^{-1/2}\ P\ s^{-1}$, where M is the molecular mass (g mol^{-1}), and P is the pressure (Torr) upstream of the conductance-limiting orifice. For Ge(100), one monolayer (ML) = 6.23×10^{14} atoms cm^{-2}, and is used below to scale doses and surface coverages.

All coverages were determined by TPD. A coverage calibration for surface hydrogen was obtained by TPD of H_2S, whose adsorption as H + SH[8] saturates at 0.5 monolayer (ML),[9] and which yields exclusively H_2 and GeS upon heating.[5] HX (X = Cl or Br) coverages were determined by assuming that both molecules similarly reach a saturation coverage of 0.5 ML of adsorbed H atoms and X atoms.

The most reproducible TPD results were obtained by operating the UHV chamber with the titanium sublimation pump saturated, which degraded the operating pressure of the chamber to 7-8 × 10^{-10} Torr but kept the pumping speed very nearly constant. After dosing, when the background pressure returned to this value, the sample was rotated to face the entrance slit of the water-cooled QMS shroud and heated at rate of 2 K s^{-1}, and the signal from the mass spectrometer was digitized by an AT-compatible personal computer.

RESULTS

Three desorption products were observed following exposure to HX (X = Cl or Br): HX, H_2, and GeX_2, as shown in Figs. 1 and 2 for HCl and HBr, respectively. In both cases H_2 desorption occurs near 570 K after a saturation dose, as for desorption from adsorbed hydrogen alone, with T_p increasing to ≈575 K at initial coverages of ≈0.05 ML. The desorption of H_2 produced by decomposition of HX is very similar to that observed following a dose of atomic hydrogen alone.[10,11]

The dependence of T_p for the H_2 and HX desorption peaks on initial HX coverage is shown in Figs. 3 and 4 for HCl and HBr, respectively. HCl and HBr desorption occurs near 578 and 582 K at saturation initial coverage, respectively, with T_p increasing by 10-20 K at initial coverages of ≈0.05 ML. The weak dependence of T_p on initial coverage for both H_2 and HX desorption, together with the asymmetric peak shapes (Figs. 3, 4), indicates near-first-order kinetics. The dihalide etch products $GeCl_2$ and $GeBr_2$ desorb at higher temperatures, 675 and 710 K, respectively, following saturation HX doses. In contrast to the behavior of the H_2 and HX TPD peaks, T_p for the GeX_2 peaks rose by 50-60 K at lower initial coverages, indicating approximately second-order kinetics.

Stoichiometry implies that for every H_2 molecule that desorbs, the two X atoms remaining from dissociative adsorption of HX must desorb as GeX_2. The desorption peaks for H_2 and HX have a strong overlap while those of GeX_2 occur at higher temperature. Therefore, the branching ratio (H_2 + GeX_2 versus HX desorption) may be usefully described by the fraction of adsorbed hydrogen atoms which desorb as H_2. This fraction is nearly coverage-independent at 0.6 for HCl, whereas for HBr it increases from 0.66 at saturation initial coverage to approximately 0.9 in the low initial-coverage limit.

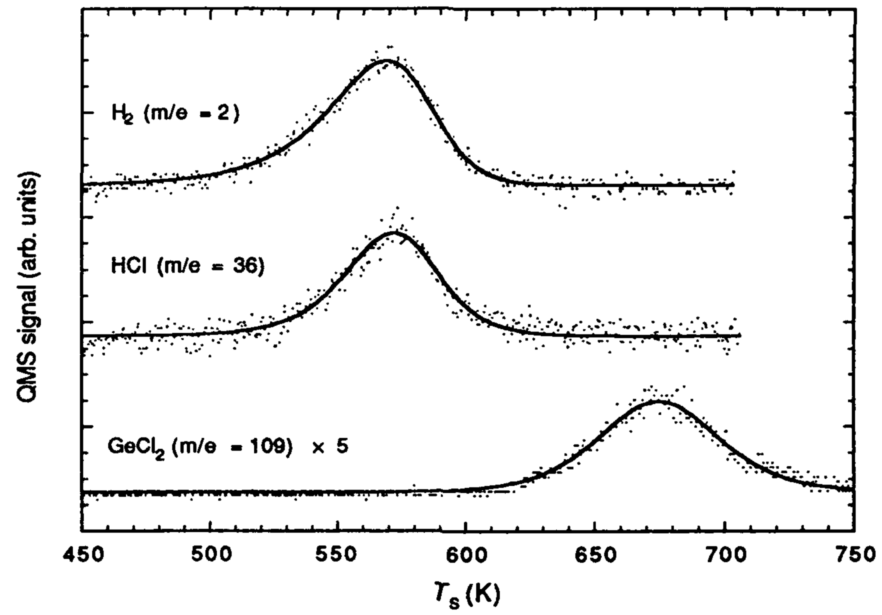

Fig. 1. Temperature-programmed desorption (TPD) spectrum of desorption products from Ge(100) following a saturation dose of HCl. Improved signal-to-noise ratio was achieved by monitoring the $GeCl^+$ cracking fraction of $GeCl_2$.

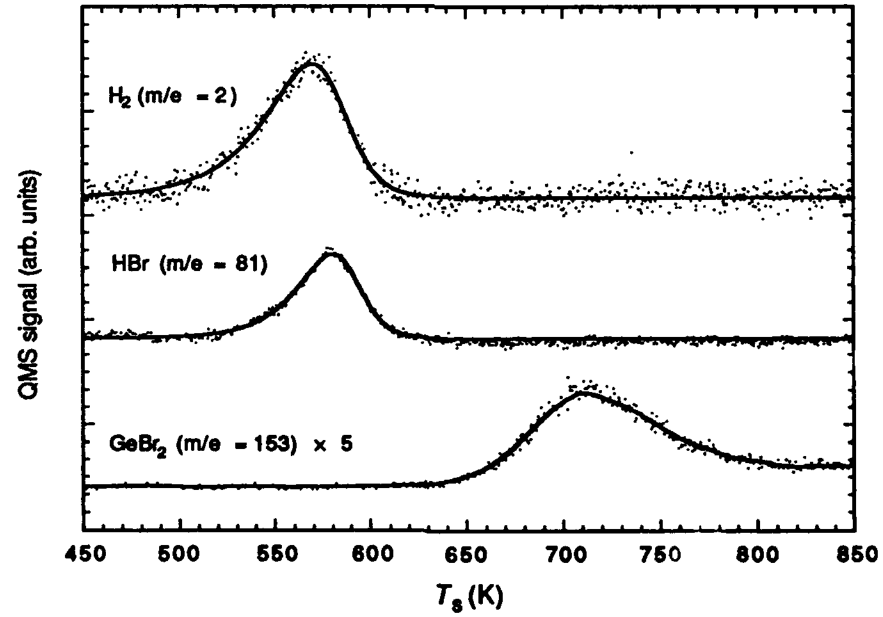

Fig. 2. TPD spectrum of desorption products from Ge(100) following a saturation dose of HBr. Improved signal-to-noise ratio was achieved by monitoring the $GeBr^+$ cracking fraction of $GeBr_2$.

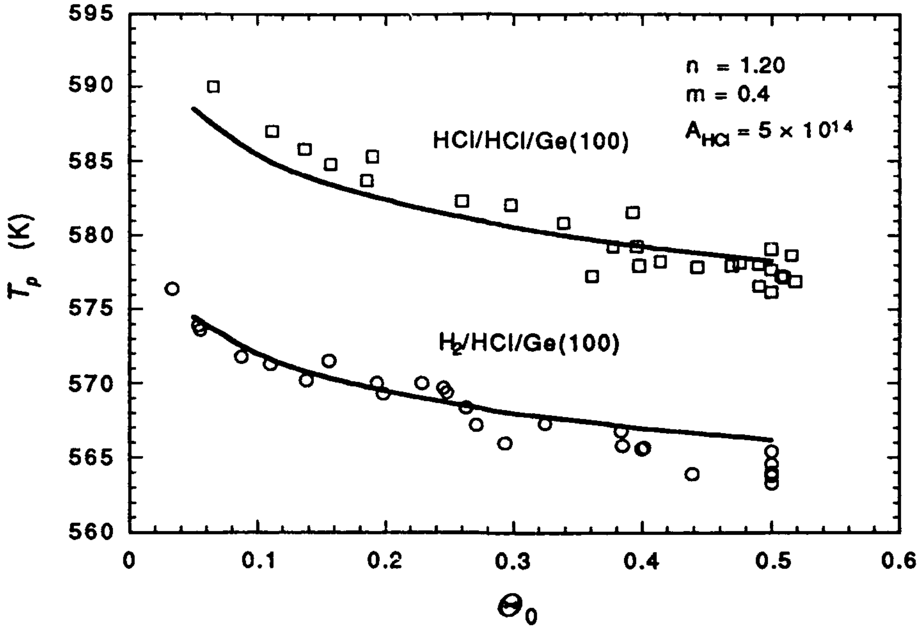

Fig. 3. Dependence of TPD peak temperatures for H_2 and HCl on initial coverage Θ_0 of adsorbed H atoms and Cl atoms.

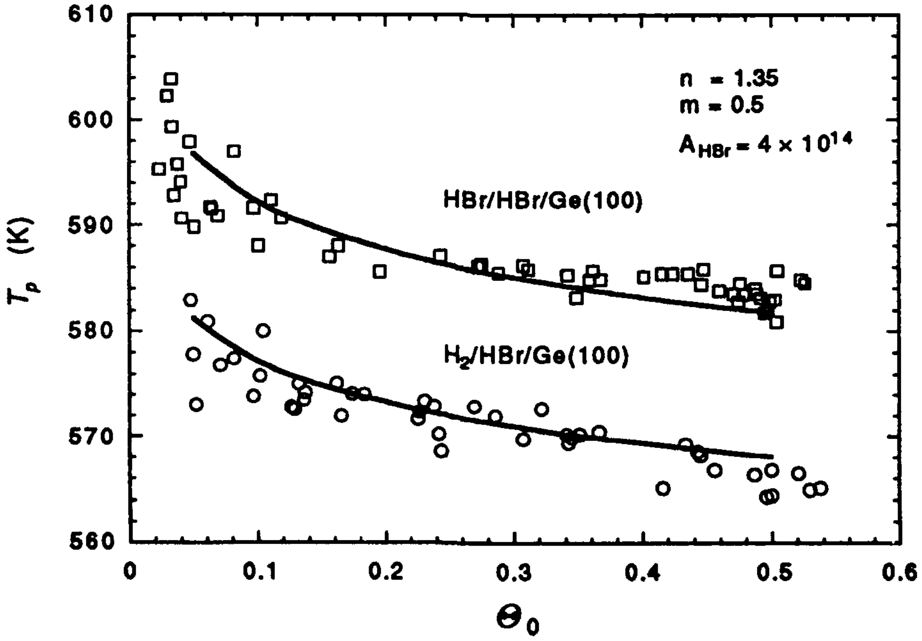

Fig. 4. Dependence of TPD peak temperatures for H_2 and HBr on initial coverage Θ_0 of adsorbed H atoms and Br atoms.

DISCUSSION

The near-first-order desorption kinetics of HX are qualitatively similar to the desorption behavior of hydrogen on Ge(100)2×1[10,11] and on Si(100)2×1.[12-15] We attribute the near-first-order kinetics to preferential pairing of adsorbed atoms on surface dimers due to the existence of weak π bonds on clean surface dimers.[14,16] We have proposed a doubly-occupied dimer model that quantitatively accounts for the desorption kinetics on both Si(100)[13-15] and Ge(100)[11] and have suggested that preferential pairing is a general phenomenon on group IV (100)2×1 surfaces.[14] The rigorous generalization of the doubly-occupied dimer model to the case of competitive pairing is discussed elsewhere.[17] Here we restrict our attention to the question of whether the desorption kinetics of HCl and HBr indeed provide evidence for preferential pairing of H+X.

We consider a simple phenomenological model for competitive desorption of H_2 and HX. We assume that the desorption rates of H_2 and HX are given by $k_{H_2}\Theta_H{}^n$ and $k_{HX}\Theta_H{}^m\Theta_X$, respectively, where k_{H_2} and k_{HX} are desorption rate constants, Θ_H and Θ_X are the instantaneous surface coverages of H and X, and n and m are phenomenological reaction orders. Random adsorption of H and X atoms should yield n=2 and m=1, whereas preferential pairing of H+H and/or H+X should produce smaller values of n and m, respectively. The rates of change of the surface hydrogen and halogen coverages during desorption are given by

$$-\frac{d\Theta_H}{dt} = k_{H_2}\Theta_H{}^n + k_{HX}\Theta_H{}^m\Theta_X \tag{1}$$

$$-\frac{d\Theta_X}{dt} = k_{HX}\Theta_H{}^m\Theta_X. \tag{2}$$

We have simulated the TPD results summarized in Figs. 3 and 4 using the fourth-order Runge-Kutta method to numerically integrate equations (1) and (2). We assumed the same kinetic parameters for k_{H_2} as for the case with hydrogen adsorbed alone, i.e., a pre-exponential factor of 2×10^{15} and an activation energy of 42 kcal/mol.[11] The activation energy of k_{HX} was assumed to be 42 kcal/mol because the TPD peak temperatures, T_p, of HX are very close to those for H_2. Initially we set $m = 1$ and $n = 1$ or 2, and the pre-exponential factor, A_{HX}, of k_{HX} was allowed to vary. We were unable to reproduce the observed variations in the peak temperature with initial coverage unless the HX yield was allowed to become very small so that $\Theta_H << \Theta_X$ and the desorption of HX became pseudo-first-order. Therefore, we fit the experimental data empirically by varying all three parameters, namely, m, n, and A_{HX}. The best fits are shown as solid lines in Figs. 3 and 4, with the fitting parameters displayed in the upper right-hand corners. The hydrogen desorption yields, defined as the ratio of the number of hydrogen atoms desorbed as H_2 to the number of initially adsorbed hydrogen atoms, fell in the range of 0.6-0.7 for both HBr and HCl, in approximate agreement with our experimental findings. The observation that the trends in T_p for HX desorption can only be accounted for with values of m less than one (0.4-0.5) indicates that adsorption of X atoms is *not* random with respect to H, but that H and X atoms preferentially pair just as do H atoms with other H atoms.

We also fitted the H_2 TPD peak temperatures from the H/Ge(100) system[11] for comparison using the same empirical method. The desorption order, n, was found to be approximately 1.08, indicative of near-first-order kinetics, which again indicates preferential pairing of H atoms. The value of n with coadsorbed Cl or Br was larger, 1.20 and 1.35 for HCl and HBr adsorption, respectively. This increase in n from the case with adsorbed hydrogen only is readily explained by the existence of competing pairing processes on the surface dimers (H+X versus H+H).

The observation of preferential pairing of hydrogen and halogen atoms on Ge(100) provides support for our prediction[14] that this is a general phenomenon, not restricted to hydrogen, and has consequences for chemical vapor deposition and atomic layer epitaxy–surface dangling-bond sites suitable for adsorption of precursor molecules will tend to occur in pairs. The presence of two types of atoms (H, X), three types of pairing (H+H, H+X, X+X), and three desorption channels necessitates a generalization of the doubly-occupied dimer model, which is currently under investigation. The pairing enthalpy for H+X need not be precisely equal to that for H+H (≈5 kcal/mol), however, because of the likelihood of steric and electrostatic interactions and bond polarization effects.

ACKNOWLEDGMENTS

The authors acknowledge the Office of Naval Research for support of this work and the National Science Foundation (Grant CHE-8715812) for additional support.

REFERENCES

1. J. Nishizawa, K. Aoki, S. Suzuki, K. Kikuchi, J. Electrochem Soc. **137**, 1898 (1990).
2. T. I. Hukka, R. I. Rawles, and M. P. D'Evelyn, Thin Solid Films (in press).
3. P. A. Coon, P. Gupta, M. L. Wise, and S. M. George, J. Vac. Sci. Technol. A **10**, 324 (1992).
4. J. A. Yarmoff, D. K. Shuh, T. D. Durbin, C. W. Lo, D. A. Lapiano-Smith, F. R. McFeely, and F. J. Himpsel, J. Vac. Sci. Technol. A **10**, 2303 (1992).
5. S. M. Cohen, Y. L. Yang, E. Rouchouze, T. Jin, and M. P. D'Evelyn, J. Vac. Sci. Technol. A **10**, 2166 (1992).
6. S. M. Cohen and M. P. D'Evelyn, J. Vac. Sci. Technol. A **9**, 2414 (1991).
7. V. T. Smith, L. M. Struck, and M. P. D'Evelyn, to be published.
8. K. T. Leung, L. J. Terminello, Z. Hussain, X. S. Zhang, T. Hayashi, and D. A. Shirley, Phys. Rev. B **38**, 8241 (1988).
9. H. J. Kuhr, W. Ranke, and J. Finster, Surf. Sci. **178**, 171 (1986).
10. S. M. Cohen, T. I. Hukka, Y. L. Yang, and M. P. D'Evelyn, Thin Solid Films (in press).
11. M. P. D'Evelyn, S. M. Cohen, E. Rouchouze, and Y. L. Yang, submitted to J. Chem. Phys.
12. K. Sinniah, M. G. Sherman, L. B. Lewis, W. H. Weinberg, J. T. Yates, Jr., and K. C. Janda, J. Chem. Phys. **92**, 5700 (1990).
13. M. L. Wise, B. G. Koehler, P. Gupta, P. A. Coon, and S. M. George, Surf. Sci. **258**, 166 (1991).
14. M. P. D'Evelyn, Y. L. Yang, and L. F. Sutcu, J. Chem. Phys. **96**, 852 (1992).
15. U. Höfer, L. Li, and T. F. Heinz, Phys. Rev. B **45**, 9485 (1992).
16. J. J. Boland, Phys. Rev. Lett. **67**, 1539 (1991).
17. Y. L. Yang, S. M. Cohen, and M. P. D'Evelyn, in preparation.